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# Evaluation of the EPA Reference Method for Measurement of Non-Methane Hydrocarbons

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# EVALUATION OF THE EPA REFERENCE METHOD FOR MEASUREMENT OF NON-METHANE HYDROCARBONS

by

J. W. Harrison
M. L. Timmons
R. B. Denyszyn
C. E. Decker

Research Triangle Institute
Research Triangle Park, N. C. 27709

Contract No. 68-02-1800

Project Officer
E. Carol Ellis
Quality Assurance Branch
Environmental Monitoring and Support Laboratory
Research Triangle Park, N. C. 27711

NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N. C. 27711

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# FOREWORD

Ambient monitoring of the criteria pollutants as well as other harmful trace contaminants is necessary for an assessment of the degree of improvement or deterioration of the environment. The Quality Assurance Branch of the Environmental Monitoring and Support Laboratory contributes to the ambient monitoring efforts by:

- evaluating analytical and monitoring techniques to determine their precision and accuracy, and
- testing the performance of analytical laboratories involved in air pollution measurements.

These activities are aimed directly at the estimation of the quality of ambient monitoring data collected by various local, state and federal pollution control agencies.

Several problems with the measurement of non-methane hydrocarbons (NMHC) using the EPA reference method have been reported. The nature of these problems are such that the validity of ambient measurements at the National Ambient Air Quality Standard level of 0.24 ppm is questionable. The research program reported herein provides an analysis of the sources of error in the measurement of NMHC by the reference method and makes recommendations for minimization of these errors with the current instrumentation.

John B. Clements, Ph.D.
Chief
Quality Assurance Branch
Environmental Monitoring and
  Support Laboratory

# ABSTRACT

Many problems have been reported with the method and instruments presently used to monitor ambient air hydrocarbons. The study reported here was carried out to determine, if possible, the sources of error inherent with the present technique and to make recommendations as to what modifications can be made to eliminate or minimize these errors. A flame ionization detector and gas chromatographic instrument were designed, built and evaluated to determine the effects of operating parameters on hydrocarbon response and the differences in response to various non-methane hydrocarbon (NMHC) species. This instrument was then used in a comparative evaluation with five commercial instruments. The evaluation included determinations of calibration stability and response to various NMHC species. Following measurements with gases from cylinders from commercial sources, the commercial instruments were further compared in a three day test using ambient air. Calibration stability was found to be reasonable, with span shifts of greater than 5% the biggest problem. There were wide differences in responses to different NMHC species. These differences were somewhat reduced by using propane response as the basis of calibration rather than methane. When ambient air was analyzed there were large discrepancies between analyzer readings which appeared to be related to atmospheric water vapor content. Recommendations are made for changes in technique to minimize analyzer discrepancies.

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# SECTION 1

## INTRODUCTION AND SUMMARY

The EPA Reference Method for non-methane hydrocarbon (NMHC) measurement (1) is summarized in Figures 1 and 2. Numerous operating problems have been reported in the field application of this method. Some of these problems are summarized in Figures 3, 4 and 5 which gives the experience of Research Triangle Institute (RTI) personnel (2), an independent contractor survey (3), and an in-house EPA evaluation (4).

In response to these difficulties EPA initiated the research program reported here to determine experimentally the critical instrumental variables which affect the response of the present Reference Method for NMHC measurement and to make recommendations to improve the capability of obtaining a uniform response to NMHC when performed by different operators using different instruments at various geographical locations.

The research was carried out in several phases. First a flame ionization detector (FID) was designed. The design was based upon a literature review, prior RTI experience, and a comparison to existing commercial designs. This FID was then evaluated to determine the effect of various operating parameters upon response to methane ($CH_4$); Section 4 details the design and evaluation.

The next phase was to design, fabricate and evaluate a gas chromatograph (GC), used with the well characterized FID, employing both the stripper column technique of the Federal Reference Method (1) and a backflush technique. Response to methane and various NMHC species were determined as well as the effect of oxygen and water vapor partial pressure variations. Section 5 details the design and evaluation of this phase.

Following this evaluation the results were summarized in a report distributed to six manufacturers of commercial instruments for NMHC analysis along with a list of questions relative to operating parameters and calibration procedures to which answers were solicited. Responses to these are discussed and compared in Section 6. Also presented in this section is a review of the design and fabrication features of representative commercial instrument models.

A comparative evaluation of five commercial analyzers as well as the RTI GC-FID was carried out. The objective was to determine calibration stability and response to specific NMHC species as well as to determine operational characteristics and problems. This evaluation is described in Section 7. Based on this comparative evaluation, the manufacturers survey, the evaluation of the RTI instrument as well as prior experience of RTI and others, an analysis of sources of error is presented in Section 8.

Conclusions based on this research are presented in Section 2 and recommendations are given in Section 3. Part of these recommendations involve a proposed Standard Method for Non-Methane Hydrocarbon Measurement, which is given in an Appendix to this report.

As a separate task on this project a draft Technical Assistance Document for Non-Methane Hydrocarbon Measurement was prepared. It will serve as a basis for a document to be subsequently released through EPA.

## REFERENCE METHOD FOR NMHC MEASUREMENTS

### Instrument Performance

**Principle**

1. Inject sample air directly into FID to measure THC.
2. Inject sample air through a stripper column into FID to measure $CH_4$. (Measurement of CO via methanator.) Backflush stripper column to atmosphere following elution of $CH_4$ and CO.

**Available Instruments**

Readout Mode - a) chromatogram
b) bargraph with automatic zero and span adjustment

Data Retrieval - NMHC = THC (peak height) - $CH_4$ (peak height)

Range - Atmospheric: THC - 20 ppm Full Scale (F.S.)
$CH_4$ - 10 ppm Full Scale
Special: THC - 2 ppm Full Scale
$CH_4$ - 2 ppm Full Scale

Minimum Detectable
Concentration - Atmospheric: 0.1 ppm equiv. $CH_4$
Special: 0.025 ppm equiv. $CH_4$

**Precision** 0.5% F.S. (0.1 ppm) on 20 ppm range

**Accuracy** 1% F.S. (0.2 ppm) on 20 ppm range
2% F.S. (0.04 ppm) on 2 ppm range

**Stability** Should meet specification with ambient temperature variations of ±3°C.

Figure 1. Instrument requirements of present Federal Reference Method (1).

## REFERENCE METHOD FOR NMHC MEASUREMENTS

### Reagents

FID Support Gas - Air with <2 ppm equiv. $CH_4$

Fuel - Hydrogen with <0.1 ppm equiv. $CH_4$

Carrier Gas - Air, $N_2$, $H_2$ or He with <0.1 ppm equiv. $CH_4$

Zero Gas - Air with <0.1 ppm equiv. $CH_4$

Calibration Gases - "Gases" with 10, 20, 40 and 80% F.S. of $CH_4$ with guaranteed certified analysis.

Span - 80% F.S. $CH_4$ in "gas".

### Calibration Procedure

Zero - Introduce zero air and electronically zero recorder pen (i.e. set baseline)

Span - Introduce span gas (nom. 80% F.S.) and set span control to proper scale reading

Calibration Curve - Introduce nom. 10, 20, 40% F.S. and check smooth curve.

Figure 2. Reagents and calibration procedure of present Federal Reference Method (1).

## OPERATIONAL PROBLEMS WITH REFERENCE METHOD

### RTI Field Experience

Variable FID/GC Response

1. Laboratory comparison of MSA, Beckman and Bendix analyzers indicated different response factors for reference samples of NMHC and $CH_4$ and for ambient air samples on instruments calibrated by procedure of the Reference Method.
2. NMHC measurements at different geographical locations were not consistent on instruments calibrated by Reference Method Procedure.

Calibration Gases

Various suppliers of compressed gases are not able to provide accurately known calibration mixtures containing methane and/or other components in hydrocarbon free air. The oxygen content of calibration gases is crtical i.e., blended air mixtures that deviate from the oxygen concentration of ambient air (21% $O_2$, 79% $N_2$) adversely affect the subsequent measurement of total hydrocarbon.

Effect of Moisture

The total hydrocarbon measurement is depressed by moisture, often producing negative non-methane hydrocarbon measurements.

Accuracy

Inaccuracies are inherent with the subtraction of large numbers (methane) from slightly larger numbers (total hydrocarbon); with the unavailability of calibration mixtures; and with instruments for which the minimum detectable level is 25 to 50 percent of the NAAQ standard.

Gas Chromatograph

1. Changes of FID reactant gas pressure, resulting in flame instability.
2. Use of pressurized calibration gas versus sample of atmospheric pressure.
3. Deterioration of analytical column.
4. Inability to maintain stable hydrogen, combustion air, and carrier gas flow rates.
5. Mechanical problems involved with operating valves.
6. Sample loss in inlet lines and plumbing.

Figure 3. RTI field experience with NMHC Reference Method (2).

## OPERATIONAL PROBLEMS WITH REFERENCE METHOD

### RTI Field Experience (Continued)

Reliability

1. Frequent electronic and/or mechanical failures.
2. Questionable operational performance due to complexity of system--60 percent valid data recovered during recent field study.

Operational Requirements

1. Requires daily attention by highly competent operator.
2. Frequent calibration required due to span drift in excess of specifications.
3. Maintenance and/or repairs generally require skilled personnel knowledgeable in electronics and gas chromatography.
4. Expensive and costly to operate.

Figure 3 (Continued). RTI field experience with NMHC Reference Method (2).

## OPERATIONAL PROBLEMS WITH REFERENCE METHOD

### Scott Environmental Report

**Coverage**

Survey of 16 users of Reference Method.

| | | |
|---|---|---|
| 10 | Beckman | 6800 |
| 2 | Bendix | 8201 |
| 1 | Bendix | 8200 |
| 1 | MSA | 2472 |
| 1 | AID | 514 |
| 1 | Bryon | 230 |

**Results**

For an NMHC mixture near 0.24 ppm equiv. $CH_4$

| Error Range | Number of Users |
|---|---|
| 0-10% | 1 |
| 10-20% | 3 |
| 20-50% | 2 |
| 50-100% | 4 |
| >100% | 6 |

**Reasons**

1. Failure of operators to understand or follow the instrument manufacturers' operating instructions and the reference method procedures for NMHC as specified in the code of Federal Regulations.
2. Span gases containing unknown amount of higher hydrocarbons.
3. Span gases not in air.
4. Span gases incorrectly analyzed for methane.
5. Zero errors due to sampling system contamination and lack of adequate checkout procedures.
6. Excessive instrument zero and span drift during unattended operation.

Figure 4. Independent contractor survey problems with NMHC Reference Method (3).

## OPERATIONAL PROBLEMS WITH REFERENCE METHOD
EPA Comparative Evaluation
(McElroy and Thompson)

### Coverage

| | | |
|---|---|---|
| 1 | Bendix 8201 | 0-10 ppm scale |
| 1 | MSA 11-2 | |
| 1 | Beckman 6800 | |
| 2 | Beckman 400 | |

### Procedure

$CH_4$ zero and span (80%)

Artificial atmosphere $C_2H_6/CH_4$ (1.97/0.9 ppm) and $C_2H_4/C_2H_2$ (1.9/1.9 ppm)

Side-by-side on ambient air at Durham Air Monitoring and Demonstration Facility

### Results

$C_2H_6/CH_4$ mix (4.84 equiv. $CH_4$): 4.97 (Bendix 8201) to 6.3 (Beckman 6800)

$C_2H_4/C_2H_2$ mix (7.6 equiv. $CH_4$): 4.8 (MSA) to 7.55 (Beckman 400)

Ambient Air:
1. Pair std. deviation ranges from 0.217 to 0.454 ppm and pairs give statistically different readings.
2. Individual std. deviations estimated as 0.23 ppm, comparable to ambient air standard of 0.24 ppm.

### Conclusions

1. Differences in FID response to various NMHC species are not the overwhelming source of response differences.
2. Drift, instability, precision, and repeatability errors are apparently the important causes of discrepancies.
3. The 5-10% (of 10 ppm F.S. range) measurement discrepancies commonly observed are large with respect to the normal NMHC range of 0-2 ppm and very large with respect to the 0.24 ppm standards.

Figure 5. EPA in-house evaluation of NMHC Reference Method (4).

# SECTION 2

# CONCLUSIONS

Evaluation of the RTI designed flame ionization detector (FID) and gas chromatograph (GC) for NMHC measurement established the following:

1. Response to methane was insensitive to support air flow rate over a range of 100 to 300 $cm^3/min$.
2. Normal variations in atmospheric pressure of ±5% about one atmosphere do not affect response more than ±2%.
3. Response to methane is maximized over a relatively narrow range of hydrogen and carrier air flow rates. If flow rates are set at maximum response values, fluctuations in flow of ±5% result in less than 2% variation in response. If these flow rates are initially set appreciably below the maximum response values, fluctuations in flow of ±5% can result in response variations of up to 8-10%.
4. There were significant variations in response to NMHC, on a per carbon atom basis, compared to the response to methane. These depended on the method of separation used. Although typically NMHC response was 20 to 30% lower than methane response, it was in some cases as low as 50%.
5. Response to methane varied with oxygen content of synthetic air. Below about 19% $O_2$ the response decreased rapidly with decreasing $O_2$. Above about 20% $O_2$ the response increased gradually with increasing $O_2$.
6. Response to methane increased with increasing sample dew point.

Following prototype evaluation, a comparative evaluation of this prototype and five hydrocarbon analyzers was conducted. Calibration stability and response to individual NMHC species, with and without methane background, were determined using cylinder gases. Immediately after this characterization the instruments were placed into service monitoring ambient air for three days.

The conclusions from these comparative tests are as follows:

1. Zero drift of these instruments is apparently not a significant problem.
2. Span drift in excess of 5% over a 24-hour period occurred with every instrument, ranging from about 15% to 70% of the time during a 13 day period.
3. Precision ranged from 0.03 ppm to 0.11 ppm on the methane channel and from 0.03 ppm to 0.16 ppm on THC for the instruments evaluated.
4. There were significant differences in response to NMHC both on an intra-instrument and inter-instrument basis. Typically for a given instrument the maximum deviation of NMHC response, compared to the average response of that instrument to 5 NMHC species, was about 20 to 30%. Response deviations to a given species were about the same on an instrument to instrument basis.
5. The NMHC response differences between instruments are improved somewhat by using propane response as a basis for correction, but are nevertheless still significant.
6. The field analyzers are of complicated design and construction and are subject to a variety of maintenance problems. As expected, one of the components most susceptible to malfunction is the automatic switching valve.
7. Materials of construction of gas lines as well as filters and columns can have a significant effect on some of the heavier or more reactive hydrocarbon species.
8. Instrument response to methane and NMHC is very sensitive to operating condition, primarily through fuel and carrier air flows. Changes can alter the response pattern.
9. Instruments made to agree in the laboratory through calibration with dry $CH_4$/air mixtures immediately start to display differences in response when exposed to the atmosphere.
10. Variations in instrument response to both $CH_4$ and THC are apparently related to atmospheric moisture content. The mechanisms which cause this relationship are not, at present, understood.

Very obvious and significant disagreements between analyzers monitoring ambient air cast doubt that the present design generation can provide reliable

NMHC data, particularly in the lower ranges near the EPA air quality standard of 0.24 ppm (equivalent $CH_4$).

Several problems occur with the Federal Reference Method as written. The restriction to one method, which in its application to several different designs of commercial instruments has not demonstrated satisfactory consistency and credibility of data, does not allow for the possibility that another, even several other, methods might develop which provide the basis for better measurements. Second, although some instrument performance spcifications are given, they are not definitive enough. For example at present range, lower detectable limit, precision and accuracy are specified. However, they are not specific as to how long these are to be maintained and under what conditions - whether prior to delivery and in the manufacturer's calibration set-up or on-site, continually.

A third problem is in the specification of reagent gases. There is no definition of "air". There is no requirement that the calibrating methane concentrations be in air. Although there are specifications on the total hydrocarbon content of the fuel, carrier and support gases, there are no indications as to how these gases can be checked to assure that specifications are met and maintained. Other than the THC content and the methane content, there are no specifications on the presence, absence or concentration levels of other species apt to be found in the atmosphere.

A fourth problem occurs with calibration. Presumably only dry gases are used whereas in operation on ambient air appreciable, and highly variable, water vapor concentrations occur. The calibration gas is specified as methane, although response to different NMHC species has been shown to be significantly different both on an intra- and inter-instrument basis. Furthermore the frequency of calibration checks is not specified.

A fifth problem occurs with the data reduction. Although the method depends upon a strip chart recorder there are not specifications on recorder performance or calibration. There are no specifications on record formats such as recording of zero and span levels on the strip chart, or with the strip chart, to facilitate re-checks of the data reduction. Furthermore, the method is implicitly limited to graphical analog recording and does not recognize the advent of economical, reliable and much more convenient digital data processing options.

A sixth problem is in the failure to provide for inter-station comparisons, or "round-robin" measurements in order to ascertain variability of data quality.

It should be pointed out in closing that the observations and conclusions about difficulties with the present Reference Method are made with the benefit of several years operating experience of many people (hindsight). The problems are not at all unusual in the translation of a technique developed under controlled laboratory conditions with highly individualized instruments into a field environment with mass produced instruments. That there are problems does not reflect invidiously on either the authors of the method or instrument designers and vendors. Only extensive experience could provide the groundwork for improving both the measurement technique, instrumental design and data reduction and reporting.

# SECTION 3

# RECOMMENDATIONS

Based on results of this research the following recommendations are made:

1. The cause of the effect of atmospheric water vapor (or other interferents) on NMHC analyzer response should be determined and counteracted, if possible.
2. Equivalency testing of different design approaches should include actual ambient air evaluations and not rely just on cylinder gases.
3. Digital data manipulation, presentation and logging should be used to improve accuracy and decrease data reduction time.
4. The present Federal Reference Method for NMHC measurements (40 CFR Part 50, Appendix F and appropriate portions of Part 53) should be revised to allow for the use of properly certified reference and equivalent methods. A proposed draft for such a document is included as Appendix D of this report.
5. The training of qualified NMHC analyzer operators should be augmented by a Technical Assistance Document on NMHC measurement. A draft TAD has been submitted under separate cover for issuance by EPA when suitable at some later date.
6. Calibration for NMHC response should use a correction factor based on instrument response to propane and include water vapor.

There still remains the question of whether existing commercial analyzer designs can be operated under conditions other than those now used which will improve agreement. Work, cited in Section 8, on automotive hydrocarbon emissions analysis indicate that with the proper selection of fuel mixture and flow rates response to various hydrocarbons can be made more uniform than with pure $H_2$ fuel and, further, that correlation between individual instruments _of the same type_ can be greatly improved. It is recommended that this be investigated for ambient air monitoring instruments. If this can be established, the next step would be to see whether or not this optimization can be extended to instruments of different design.

# SECTION 4

# FLAME IONIZATION DETECTOR

## DESIGN FACTORS

A thorough literature search was made before the design of the FID was decided. The parameters most influential in affecting response were determined. The design chosen allows variation of these parameters in order to assess their relative effect on hydrocarbon response.

Response of an FID to hydrocarbons is strongly affected by the magnitude and spatial distribution of the electrical potential difference between the electrodes and by the spatial configuration of the flame (5). The spatial distribution of electrical potential is determined by the geometry of the electrodes and by the presence of any insulating layers on the electrodes. The flame configuration depends upon the jet size, fuel feed and support gas flow. The basic design of the prototype FID, shown in Figure 6, is a modification of a model which has been used for work under controlled pressures (6). As shown in the circuit diagram in Figure 7 the flame tip is made positive, referenced to system ground. A positive potential on the jet reduces the noise caused by electronic emission from overheated jet tips (7). In addition it has been reported that the plateau of the current-voltage curve is more easily attained with positive jets (8), although when actually in the saturation region, response is the same for either polarity voltage on the jet (9). Both of these phenomena, electronic emission from hot jets and attainment of saturation, were verified recently by McWilliam (10).

The jet tip itself is subject to corrosion and should be constructed from an inert material. Corrosion products may be sufficiently insulating to change the potential distribution. The jet should have a high thermal conductivity to effectively conduct heat away from the flame area, and utilization of a heat sink is recommended (7). Stainless steel meets both

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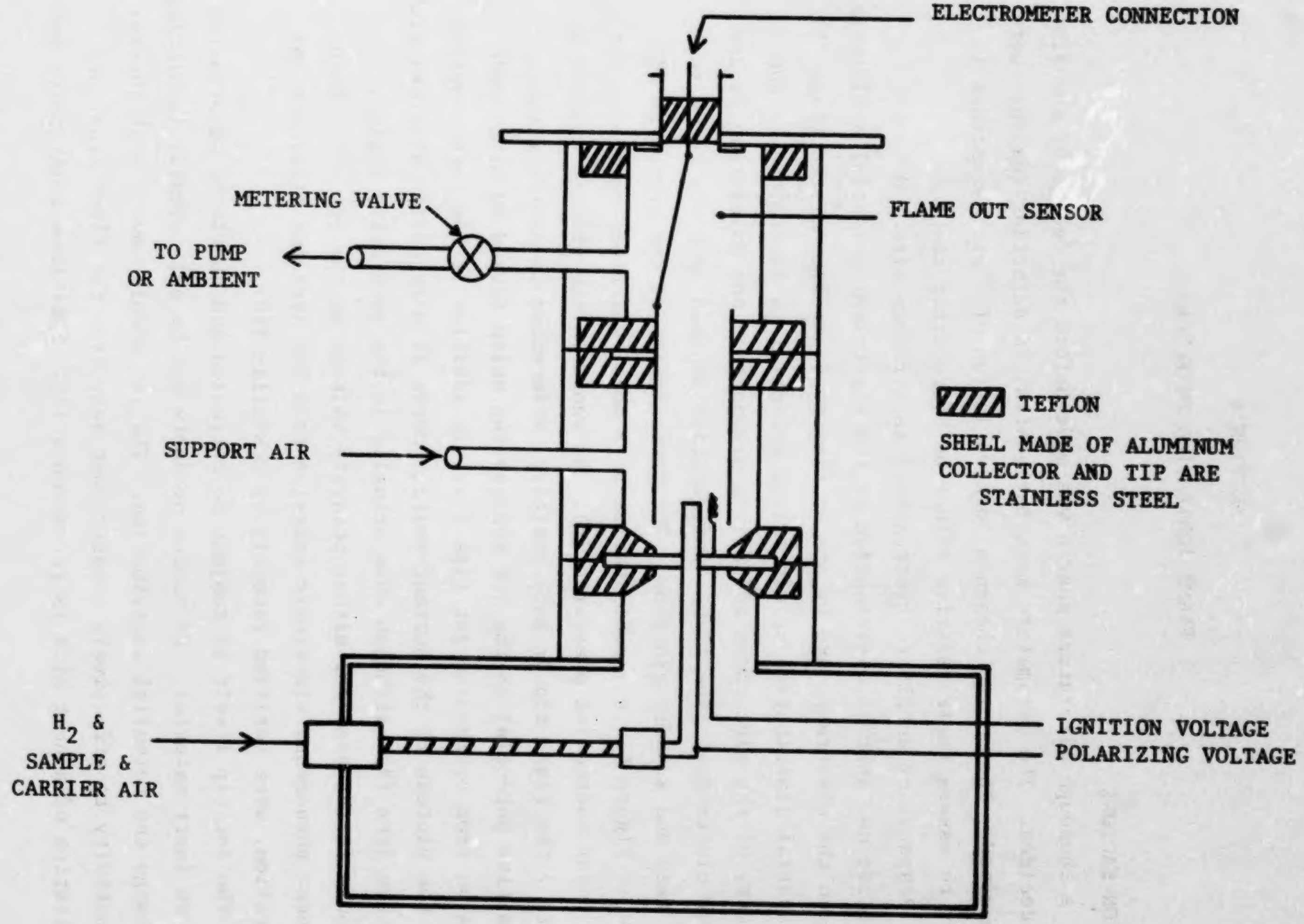
ELECTROMETER CONNECTION
METERING VALVE
FLAME OUT SENSOR
TO PUMP OR AMBIENT
▨ TEFLON
SHELL MADE OF ALUMINUM
COLLECTOR AND TIP ARE
STAINLESS STEEL
SUPPORT AIR
$H_2$ & SAMPLE & CARRIER AIR
IGNITION VOLTAGE
POLARIZING VOLTAGE

Figure 6 . Design of flame ionization detector.

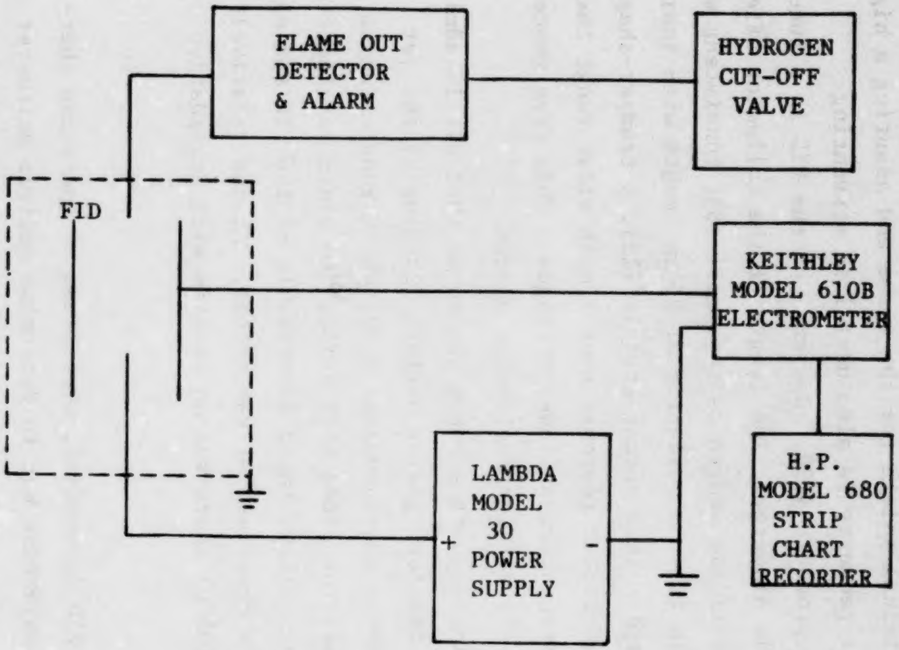
FLAME OUT DETECTOR & ALARM
HYDROGEN CUT-OFF VALVE
FID
KEITHLEY MODEL 610B ELECTROMETER
LAMBDA MODEL 30 POWER SUPPLY
+
-
H.P. MODEL 680 STRIP CHART RECORDER

Figure 7. Block diagram of FID electronics.

of these requirements. The diameter of the jet opening for the RTI design was kept to less than 0.51 mm (0.020 inch) because response has been reported to fall off sharply with larger sized openings (11).

The collector electrode was chosen to be cylindrical for several reasons. Obviously, it offers an electrical potential distribution with the same rotational symmetry as the flame. The flame tip is at a positive potential, and the FID shell is at approximately the same potential as the collector. In order to avoid leakage currents from the flame tip to the shell walls, the collector is lowered below the level of the flame, producing an effective electrical shield for the flame and assuring a high collection efficiency. This geometry is also useful in preventing recirculation of combustion products (12). Response of the FID is a function of both the length and inside diameter. The length of the collector affects the range of linear response if the length is too small (5); consistent with results from Gill and Hartman (11), a collector of 25 mm length with inside diameter of 11 mm was selected. In a recent article (13), a trumpet-shaped collector was claimed to give linear response over a much wider range than cylindrical electrodes and saturation at lower voltages. This type geometry may offer an alternative to the straight collector design.

The method of introducing support air was chosen so that air is admitted in a ring about the base of the jet, giving uniform flushing of the jet from all sides. This provides a non-turbulent flow, which reduces noise (5).

Both electrodes were well insulated with Teflon® to minimize electrical leakage and the modular design allows rapid disassembly of the FID and easy replacement of components for experimental variations. At the relatively low temperatures used (70°-105°C) there was no problem with degradation of this polymer.

## EVALUATION

With the design of the FID determined, evaluation of operating characteristics was begun. The objective was to determine optimum parameter values. A factorial test design approach (14,15) was used to select the optimum operating point. Such a test design is useful when the effect of a large number of operating parameters, many of them interacting, must be assessed without devoting an excessive amount of time to doing so. Many standard statistical test designs are available (16). A suitable evaluation sequence was designed (17) using the following variables as experimental parameters:

1. polarizing voltage,
2. sample concentration,
3. hydrogen flow rate,
4. carrier air flow rate,
5. support air flow rate, and
6. pressure.

Details of the test design are given in Appendix A. All of these factors have been shown to influence the response of the FID. The gas flow and polarizing voltage effects can be found in any comprehensive study of FID performance (5,10,17, for example). The role of pressure in optimum FID operation has been less well studied although it has been shown that normal atmospheric fluctuation can result in response variations as large as 6% (6). Provisions were made, therefore, to control the pressure by placing a needle valve in the exit gas port of the FID. Subambient pressures were achieved by connecting the exit gas port through this valve to a vacuum pump. The sample size dependence is a measure of the linearity of a particular FID and does vary with design from manufacturer to manufacturer (14).

The physical arrangement used for the FID evaluation is shown in Figure 8. The chamber was controlled at a constant (±0.5°C) temperature of 70°C. Flow and electrical circuit arrangements were as sketched in Figure 9. Support and carrier air were obtained from breathing grade compressed air from which hydrocarbons were removed by passing over a catalyst bed containing palladium coated on 3 mm (0.125 inch) alumina spheres maintained at 280°C. Previous experience with this type of clean-up had yielded THC contents of less than 50 ppb. Water vapor and $NO_x$ were removed by passing the exit stream over drierite and potassium permanganate beds. Hydrogen was obtained from ultra-pure grade compressed $H_2$ with a certified THC content less than 100 ppb. A needle valve restrictor was used in the sample inlet line to the FID to suppress pressure surges.

Coded experimental values of the variables and the resulting response values that resulted are given in Appendix A. These were used in a multiple regression analysis program. Plots of the mean values of FID signal current versus the variable values are shown in Figures 10 through 15.

NOTE: DOOR NOT SHOWN

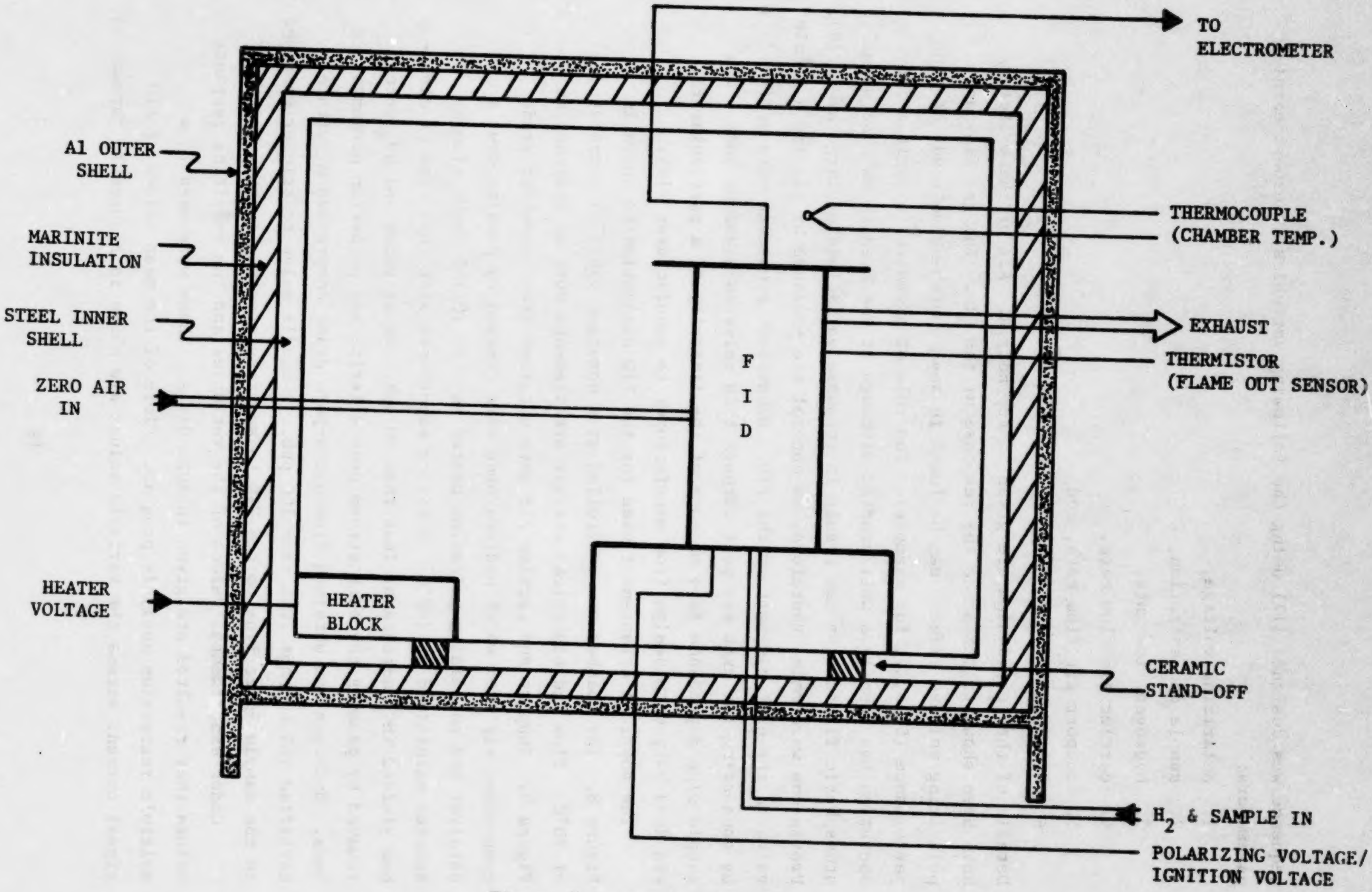
TO
ELECTROMETER
Al OUTER
SHELL
MARINITE
INSULATION
STEEL INNER
SHELL
ZERO AIR
IN
HEATER
VOLTAGE
HEATER
BLOCK
F
I
D
THERMOCOUPLE
(CHAMBER TEMP.)
EXHAUST
THERMISTOR
(FLAME OUT SENSOR)
CERAMIC
STAND-OFF
$H_2$ & SAMPLE IN
POLARIZING VOLTAGE/
IGNITION VOLTAGE

Figure 8. FID test chamber.

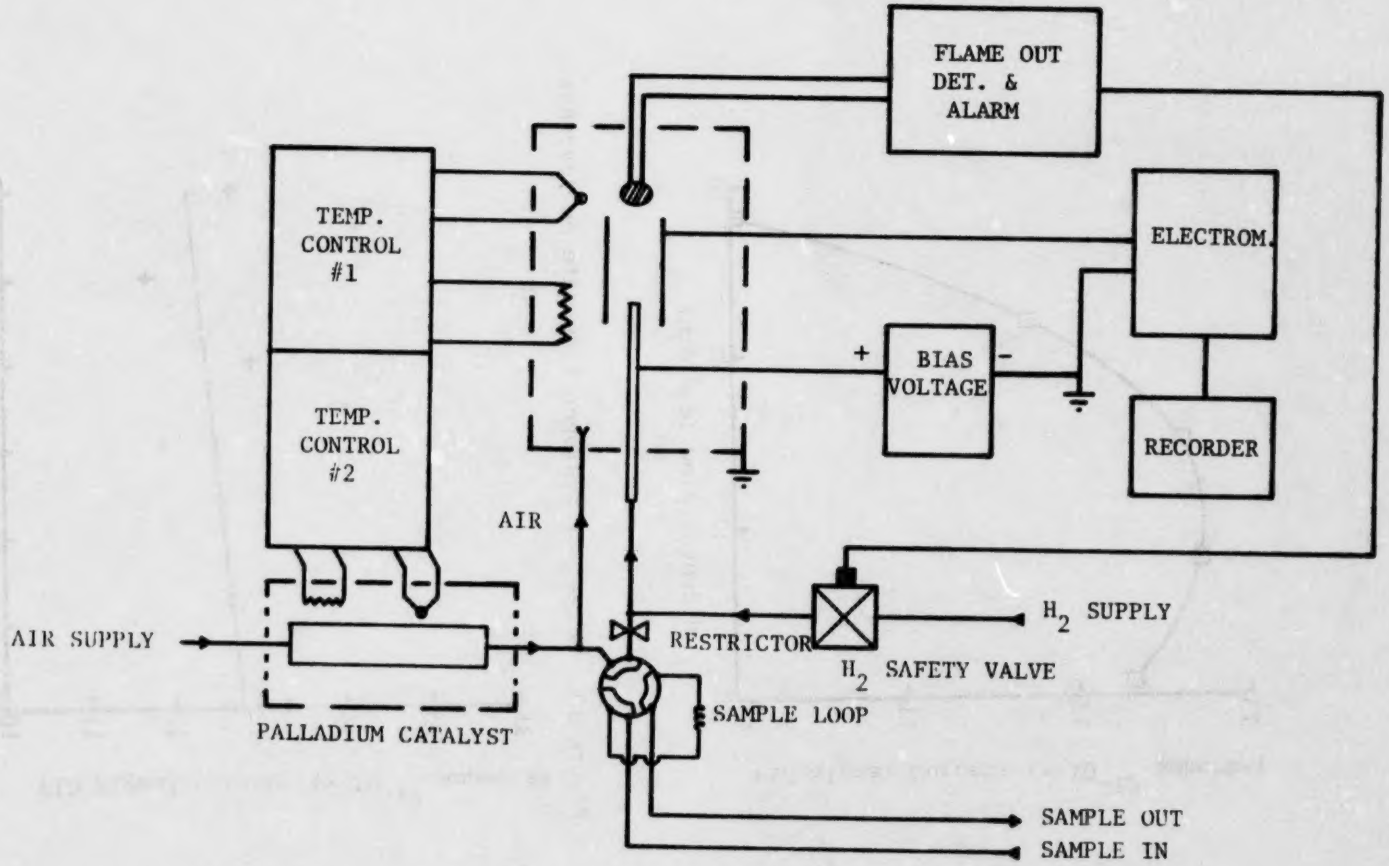
FLAME OUT
DET. &
ALARM
TEMP.
CONTROL
#1
TEMP.
CONTROL
#2
ELECTROM.
BIAS
VOLTAGE
+
-
RECORDER
AIR
AIR SUPPLY
PALLADIUM CATALYST
RESTRICTOR
H2 SAFETY VALVE
H2 SUPPLY
SAMPLE LOOP
SAMPLE OUT
SAMPLE IN

Figure 9. Block diagram of FID test set-up.

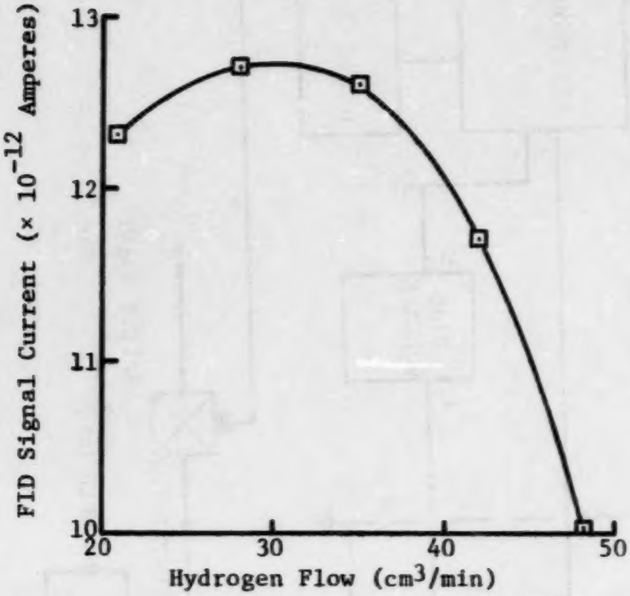

Figure 10. Effect of hydrogen flow rate on response.

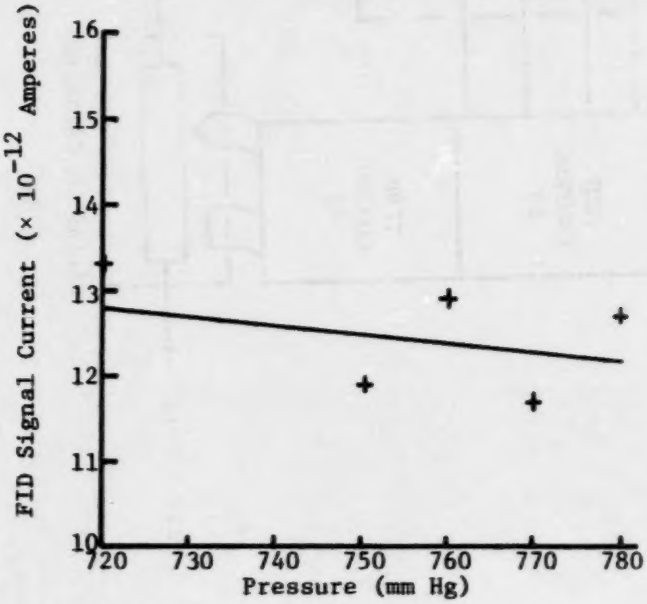

Figure 11. Effect of FID pressure on response.

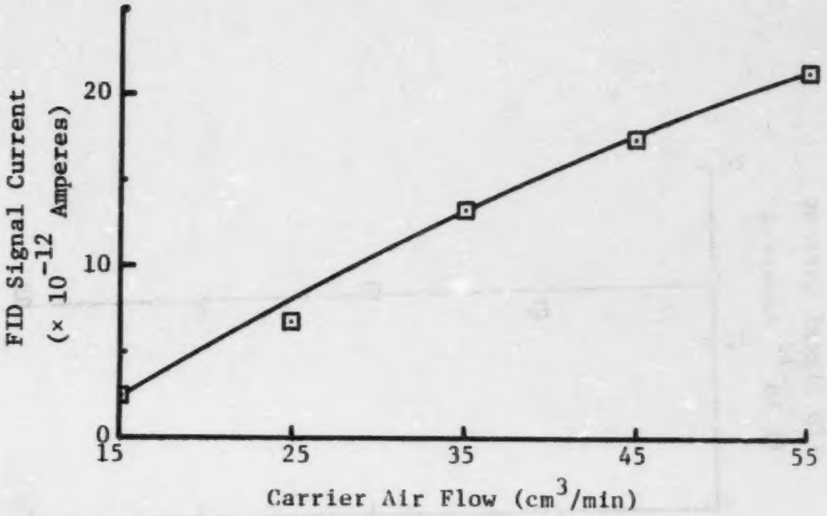

Figure 12. Effect of carrier air flow on response.

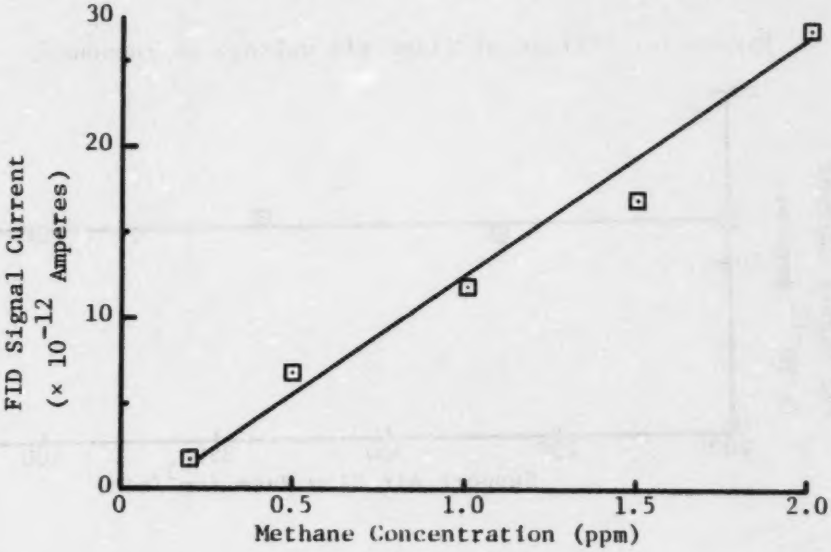

Figure 13. Linearity of FID response to methane.

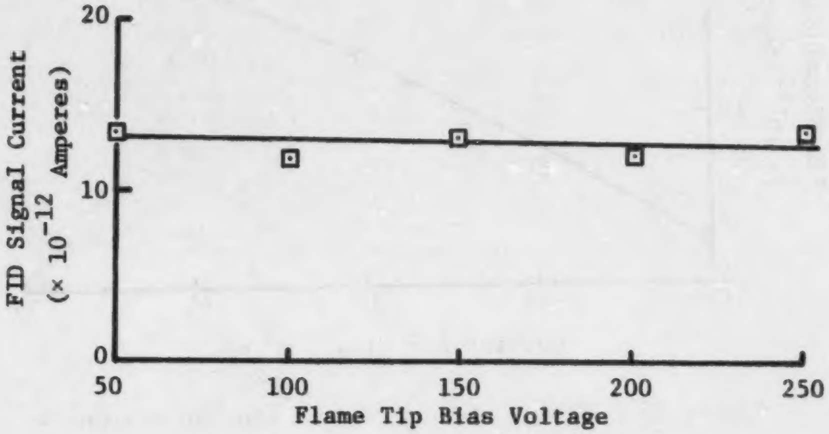

Figure 14. Effect of flame tip voltage on response.

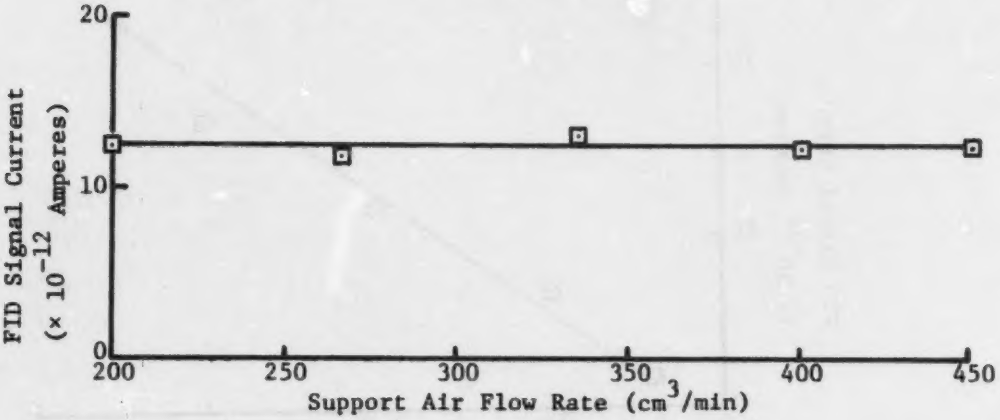

Figure 15. Effect of support air flow rate on response.

A mathematical model for the response surface which includes second order and interaction terms, was obtained from a multiple regression analysis, described in Appendix A. Application of a standard Fisher test for statistical significance indicated that of all of the linear, square and crossterms (27 total), only ten or eleven could be considered influential in the range of variables used. Accordingly a reduced model was tested, using ten variables. The R-square value, a measure of how well the mathematical model fits the data of this model, was 0.98535, compared to 0.98957 for the full model, indicating that the fit was still good. For this simple model the response is given by

$$\begin{aligned} R_1 = 159.87 &- 3.24X_1 + 62.34X_3 + 66.66X_6 \\ &+ 6.61X_1X_3 - 4.43X_1X_5 - 5.79X_1X_6 \\ &- 2.15X_2X_5 + 29.95X_3X_6 - 4.81X_1X_1 \\ &- 3.04X_3X_3 \end{aligned} \tag{1}$$

where the scaled variable values are given by:

$$X_1 = [\text{hydrogen flow } (\text{cm}^3/\text{min}) - 35]/7 \tag{2}$$

$$X_2 = [\text{air flow cm}^3/\text{min}) - 333.5]/66.5 \tag{3}$$

$$X_3 = [\text{carrier flow cm}^3/\text{min}) - 35]/10 \tag{4}$$

$$X_5 = [\text{pressure (torr)} - 760]/10 \tag{5}$$

$$X_6 = 3X[\text{sample size (ppm)} - 1] \; . \tag{6}$$

In this model the Fisher test indicated that the $X_2X_5$ term was not significant and could probably be excluded. The Fisher test also indicated that an even more simple model could be used, employing only $X_3$, $X_6$ and their interaction. This approximation gave an R-square value of 0.9720, compared to the 0.98535 for the ten-term model, which is still a reasonable fit. This model is

$$R_o = 153.73 + 63.23X_3 + 68.08X_6 + 29.49X_3X_6 \; . \tag{7}$$

These response numbers can be converted to equivalent current values by multiplying by a factor of $7.87 \times 10^{-14}$ Ampere.

Sensitivity of the response to changes in hydrogen flow, carrier air flow or a change in concentration can be obtained by taking the partial derivatives of $R_1$ in equation (1) with respect to the variables $X_1$, $X_3$ and $X_6$ to obtain

$$\Delta R_1 = \left.\frac{\partial R_1}{\partial X_1}\right|_{op} \Delta X_1 + \left.\frac{\partial R_1}{\partial X_3}\right|_{op} \Delta X_3 + \left.\frac{\partial R_1}{\partial X_6}\right|_{op} \Delta X_6 \ . \qquad (8)$$

The partial derivatives are evaluated at the operating point values of the parameters. Assuming that the operating point is at a hydrogen flow of 32 $cm^3$/min selected for maximum response, a carrier air flow of 32 $cm^3$/min, an operating pressure of 760 torr, a support air flow of 350 $cm^3$/min, an electrode voltage of 100 volts and a sample size of 1 ppm $CH_4$, changes in response due to changes in the three operating variables can be calculated. Three cases will be considered.

Case 1 There is about a 10% change in hydrogen flow, 3 $cm^3$/min, with no change in carrier air flow or input concentration. Using the appropriate operating values in equations (1) and (8) gives a negligible change in response, about 0.3%.

Case 2 There is about a 10% change in carrier air flow, 3 $cm^3$/min, with no change in hydrogen flow or input concentration. This gives a 13.2% change in response, which is quite significant.

Case 3 Both hydrogen and carrier air flow are stable at the selected operating point. The sensitivity to changes in input hydrocarbon concentration is $1.42 \times 10^{-11}$ amperes/$CH_4$.

The response surface of equation (1) has quadratic terms for both the hydrogen flow and carrier air flow. The plot of mean values of response versus $H_2$ flow rate, Figure 10, shows this very clearly, but it is not apparent in the plot of mean values of response versus carrier air flow in Figure 12. However, as will be shown in the next section, quadratic dependence of response on carrier air flow was also observed.

To summarize the results of this investigation of FID response:

1. There is an optimum value of $H_2$ flow which will maximize response and minimize response variations due to flow fluctuations.
2. Response monotonically increases with carrier air flow.
3. Normal atmospheric pressure variations will cause about ±2% response variation.
4. Response is linear for methane over 0.2-2 ppm range.
5. Variation of support air flow over the range 200-470 $cm^3$/min did not affect response.
6. Variation of bias voltage of flame tip over 50-250 volt range did not affect response.

Following this evaluation this FID was incorporated into a prototype gas chromatograph design for an evaluation of operating characteristics. This is described next in Section 5.

## SECTION 5

## GAS CHROMATOGRAPH FOR NMHC MEASUREMENT

### DESIGN AND CONSTRUCTION

Having determined the operating characteristics of the FID, the design for the gas chromatograph (GC) was implemented as shown in Figure 16. Before fabrication was begun, however, chromatographers from Bendix Corporation and EPA were consulted to locate obvious design flaws, but none were indicated to RTI.

Valves #1 and #2 are zero volume, pneumatically operated valves (18). They provide the necessary switching between sample loops, $L_1$ and $L_2$, and the stripper column and restrictor, S and R. The volumes of $L_1$ and $L_2$ are matched at 3 $cm^3$ each, and R is used to match the pneumatic impedance of S when a THC determination is being made. The impedance matching is necessary to prevent baseline shifts and gas flow alteration which cause these shifts. Valve #3 allows directing the backflush air stream from the stripper column to the FID for the backflush mode of operation. Valve #4 permits selection of sample or span gas lines. Gas flows are controlled by pneumatic flow controllers which give constant gas flow with constant upstream pressure (19).

The stripper column is mounted inside the instrument oven, which is contrary to the Reference Method guideline (1). The reason for this is the nature of the stripper material, a carbon molecular sieve (20). This material has the ability to separate CO, $CO_2$ and air from methane, is not deactivated by moisture as are zeolites and is stable to over 120°C in oxidizing environments. The only disadvantage of the carbon molecular sieve is that higher molecular weight hydrocarbons ($>C_5$) are difficult to remove in the backflush mode of operation. For most of the compounds evaluated in our studies, however, this was not a serious problem.

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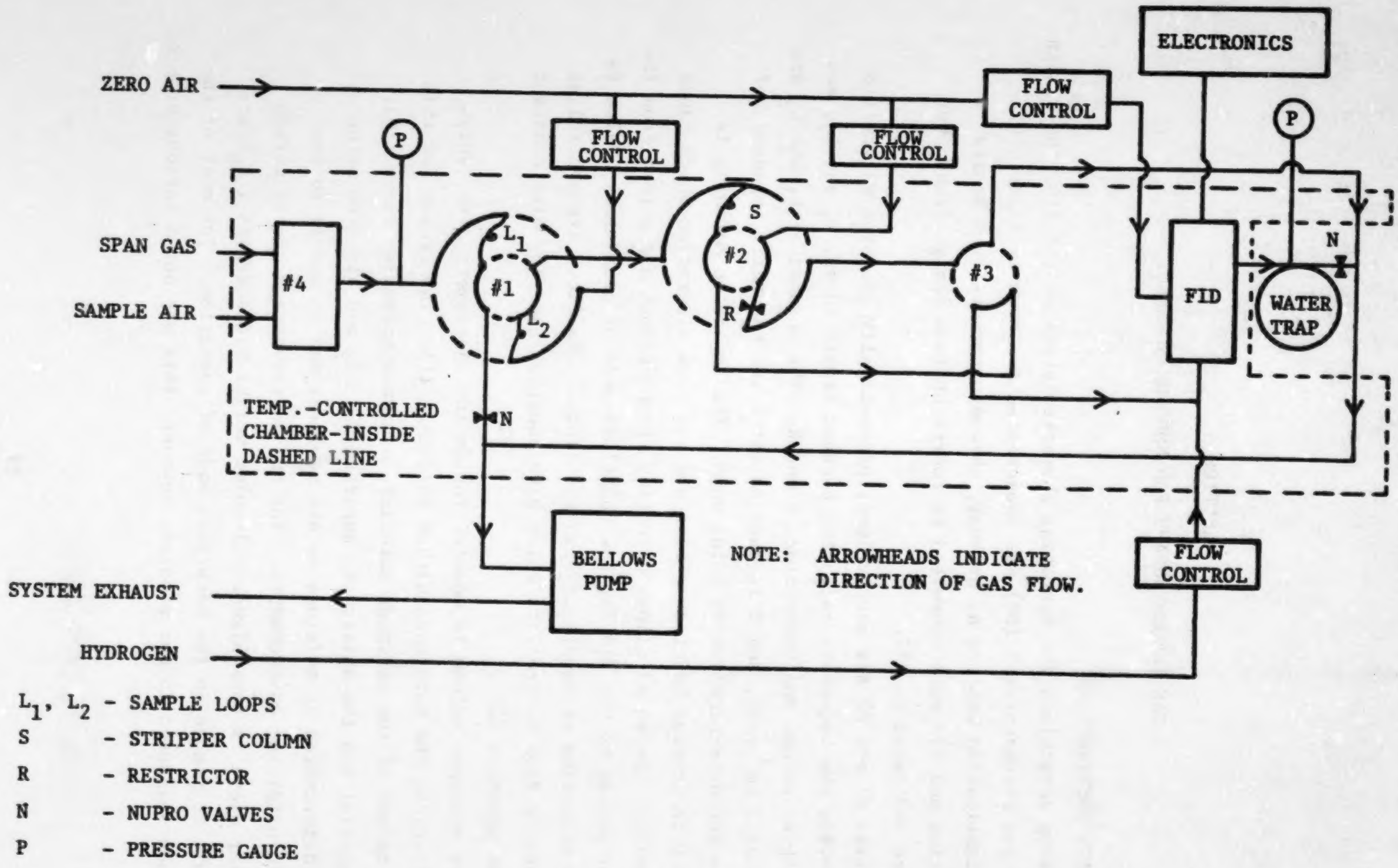
ZERO AIR
SPAN GAS
SAMPLE AIR
SYSTEM EXHAUST
HYDROGEN
ELECTRONICS
FLOW CONTROL
FLOW CONTROL
FLOW CONTROL
FLOW CONTROL
P
P
#4
#1
#2
#3
$L_1$
$L_2$
S
R
N
N
FID
WATER TRAP
BELLOWS PUMP
TEMP.-CONTROLLED CHAMBER-INSIDE DASHED LINE
NOTE: ARROWHEADS INDICATE DIRECTION OF GAS FLOW.
$L_1$, $L_2$ - SAMPLE LOOPS
S - STRIPPER COLUMN
R - RESTRICTOR
N - NUPRO VALVES
P - PRESSURE GAUGE

Figure 16. Design of gas chromatograph.

The zero air supply which was used as the carrier air and support air and for sample dilution was obtained by passing breathing quality air from tanks over a palladium catalyst bed, through a potassium permanganate bed for removal of $NO_x$ species, and finally through a drying bed to remove moisture. A similar system, in routine operation at RTI, was found to produce air with less than 50 ppb THC. Hydrogen with <0.1 ppm THC was supplied by cylinder.

## EVALUATION AND PEAKING OF METHANE RESPONSES

An evaluation procedure similar to the FID evaluation was used to determine the optimum methane response of the GC-FID combination. However, only three parameters, hydrogen flow, carrier flow, and support air flow, were varied. Because FID evaluation had shown no effect on response for polarizing voltage and little effect for pressure variations, the bias voltage was set at 100 V, and the FID was vented to the atmosphere. This test sequence is shown in Table 28 of Appendix A along with the response, (millimeters of peak height) to a 2.0 ppm sample of $CH_4$ in HC-free air (21). Each parameter being studied was varied at three levels (27 total experiments). The mean of the FID signal current was calculated at each of the levels for the three parameters, and these data are presented in Figure 17. From the data shown in Figure 17, it can be seen that FID response to methane has the following properties:

1. response is relatively insensitive to changes in support air flow in the range studied (100-300 $cm^3$/min) for this instrument design,
2. response as a function of hydrogen flow peaks at about 37 $cm^3$/min, and
3. response as a function of carrier air flow peaks at about 47 $cm^3$/min.

Comparing these results to those presented in the FID evaluation, the support air insensitivity was the same above 100 $cm^3$/min. (See Figure 15). Hydrogen effects on the response curve were identical, but the maximum shifted from about 32 $cm^3$/min for the FID alone to 37 $cm^3$/min for the FID-GC combination (Figure 10). The response as a function of carrier air flow showed no maximum when only the FID was studied (Figure 12), but peaked at 47 $cm^3$/min with the FID-GC combination.

The nature of the hydrogen and carrier air effects on the response suggested that there should be a peak in the methane response of the GC, occurring at about a hydrogen:carrier air ratio of 0.79. However actual

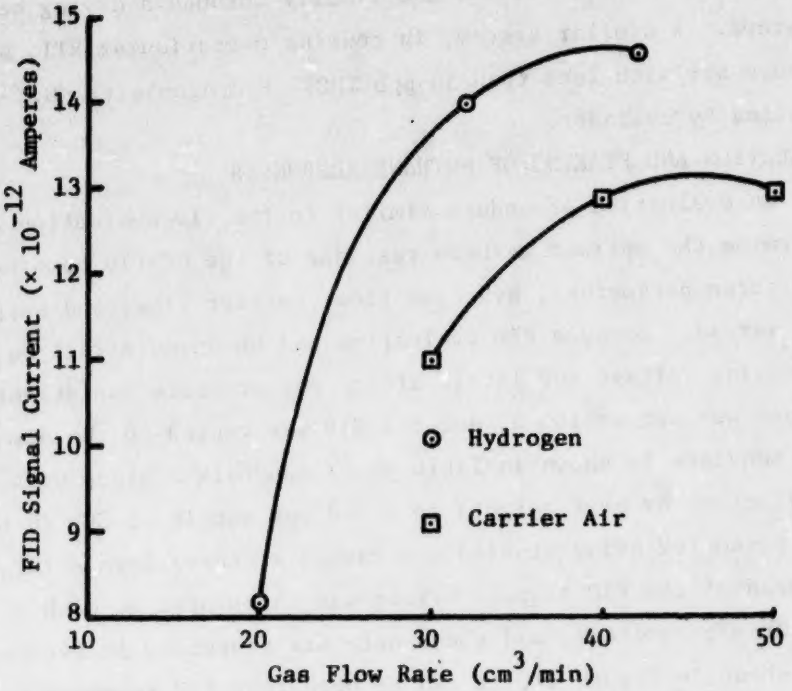

Figure 17a. Effect of hydrogen and carrier air on response.

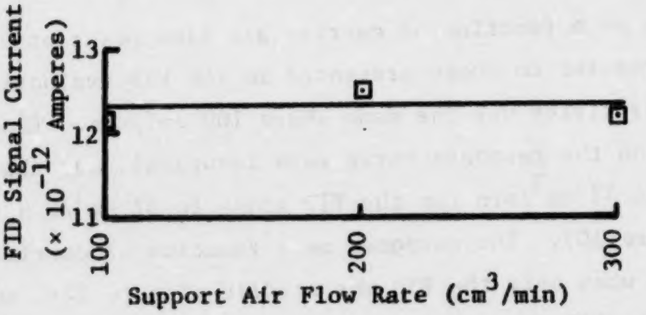

Figure 17b. Effect of support air on response.

measurement of the peaking in response, displayed in Figure 18, showed the value to be closer to 0.70. While operating at these peak response conditions (for methane), the FID-GC methane sensitivity was calculated to be $1.39 \times 10^{-11}$ amperes/ppm $CH_4$ which compared to $1.42 \times 10^{-11}$ amperes/ppm $CH^4$ for the FID alone.

For all practical purposes it appears that the characteristics of the GC-FID are determined by the detector.

## EFFECT OF SAMPLING CONDITIONS AND OXYGEN CONTENT OF REAGENT GASES

To characterize the inlet parameters two experiments were performed. In the first, the pressure at the inlet was held to $6.89 \times 10^3$ Pa (1 psi) above the ambient, and sample flow rate was varied from 10 $cm^3$/min to 100 $cm^3$/min using a constant concentration of 2.0 ppm methane. The GC was operated with the optimum hydrogen:carrier ratio (0.70) for peak methane response indicated in Figure 18 with support air flow at 150 $cm^3$/min. The response increased only slightly (<2%) with increasing methane flow rate. In the second test, the methane sample flow rate was held constant at 30 $cm^3$/min, and the inlet pressure was varied from $6.89 \times 10^{+3}$ Pa to $7.58 \times 10^{+4}$ Pa (1 psi to 11 psi) above ambient. The response increased linearly with pressure (see Figure 19) until $6.2 \times 10^{+4}$ Pa was reached. At this pressure there was an abrupt reduction in slope but the increase in response with pressure remained linear. The breakpoint most probably occurred when sample line pressure matched carrier line pressure.

The effect of using a nitrogen carrier instead of air was briefly examined. With the same operating conditions which yielded maximum in the methane response, 2.0 ppm methane sample gave a response lower than had been observed with air. However, by increasing the nitrogen flow an identical peak height to that with air was again attained, but the peak area was only 50 to 70% as large as with air.

The question of the effect of oxygen concentration in synthesized zero air on the GC-FID response to methane was then addressed. Air streams ranging from 12% $O_2$ to 27% $O_2$ were blended from nitrogen and oxygen (<0.1 ppm THC each) and were used as the carrier gas. Operating parameters were selected as previously to give near optimum methane response. The logarithm of the background current versus the oxygen percentage gave a linear relationship, as expected.

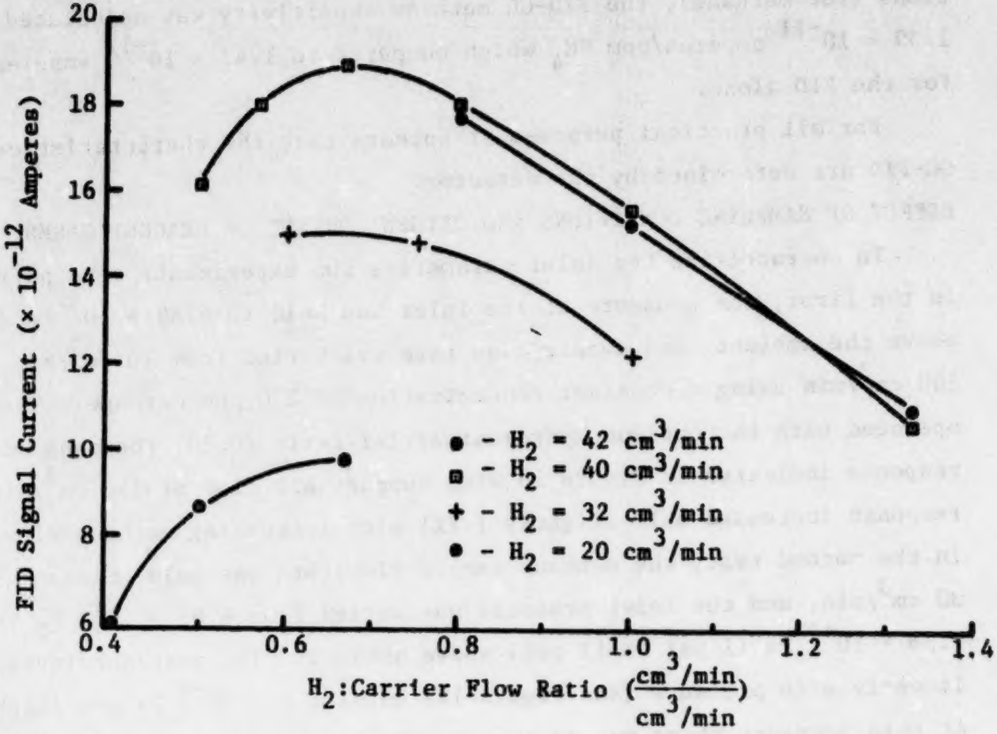

Figure 18. Effect of Fuel:Carrier Ratio on response.

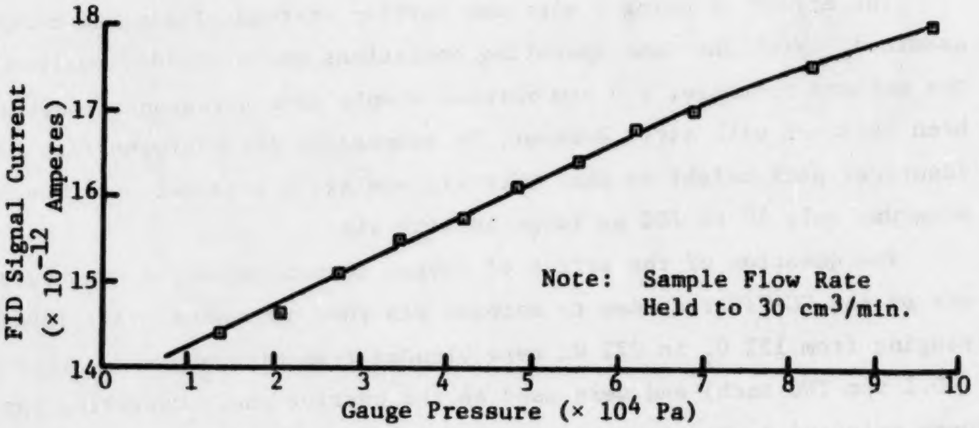

Figure 19. Effect of sample inlet pressure on response.

The effect of oxygen content on methane response is shown in Figure 20 where the peak area for each injection (obtained by digital integration) vs. % $O_2$ is plotted. The large variation in response at the lower percentage $O_2$ content suggests the need to specify a minimum $O_2$ content of about 19%. However, in the range of 19% to 23% $O_2$, the response was found to vary only 2%. No attempt was made to peak the response at each of the individual $O_2$ concentrations by flow rate adjustment as was done when investigating the effect of nitrogen as a carrier gas.

## COMPARISON TO GUIDELINE SPECIFICATIONS

The precision, span drift, noise and zero drift were determined as the final step in quantifying the operating characteristics of the prototype. To get information on precision and span drift a five day test was performed in which 2.0 ppm methane injections were made at various times during the day (approximately hourly) until a total of seven injections per day had been made. These injections were made with the GC operating with optimized response for methane. The data, shown in Table 1, include the mean and standard deviation of the peak heights of the seven daily injections measured to the nearest one-half mm. The span drift which is reported as a percent was calculated according to the definition given in EPA performance guidelines (22), and the precision was calculated as two times the standard deviation, the procedure used in the Scott Report (3). Both the precision and span drift are within the guideline values of 0.3 ppm and ±5%. The zero drift and noise values were determined by allowing the instrument to operate unattended at the methane-response optimum for two days. Using the methane

TABLE 1. DETERMINATION OF PRECISION AND SPAN DRIFT OF RTI INSTRUMENT

| Day No. | Response (mm) Mean | Response (mm) Stan. Dev. | Span Drift (%) | Precision (ppm) |
|---|---|---|---|---|
| 1 | 93 | ±2.0 | ---- | 0.09 |
| 2 | 94.5 | ±1.0 | +1.6 | 0.04 |
| 3 | 95 | ±2.0 | +0.5 | 0.08 |
| 4 | 94 | ±0.5 | -1.1 | 0.02 |
| 5 | 94.5 | ±1.0 | +0.5 | 0.02 |

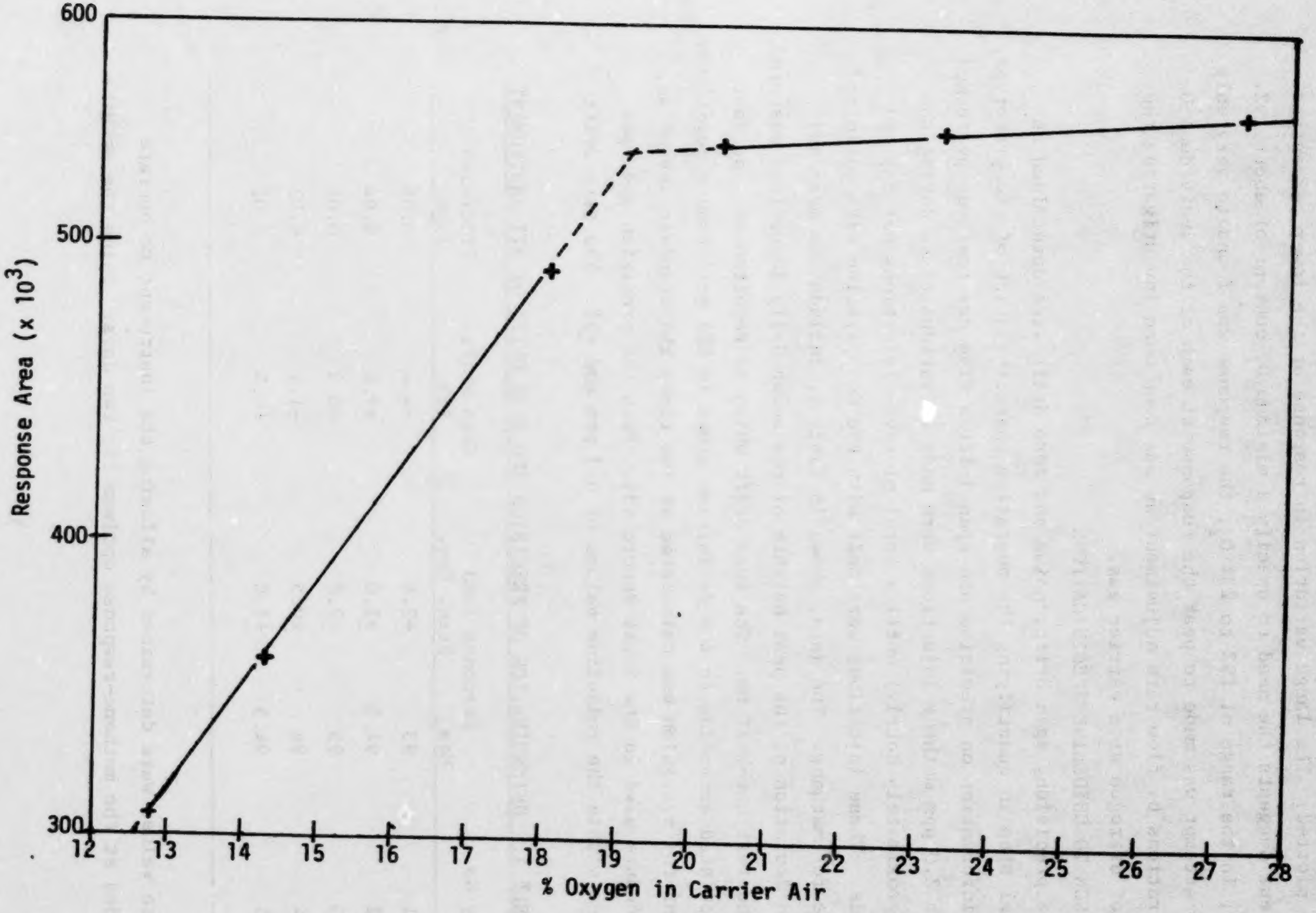

Figure 20. Dependence of response on carrier air oxygen content.

current/concentration conversion factor of $1.39 \times 10^{-11}$ amperes/ppm $CH_4$ determined previously, the zero drift and noise values were calculated and are shown in Table 2. The zero drift is broken down into 12-hour and 24-hour readings in ppm, and the noise is the maximum noise what was noted during the two, 24-hour periods. These values are also within the performance guideline (22) values of ±0.2 ppm and 0.05 ppm for zero drift and noise, respectively.

TABLE 2. ZERO DRIFT AND NOISE DATA FOR RTI GC-FID

| Period 2 | Zero Drift (ppm) | Noise (ppm) |
|---|---|---|
| 12 hr morning, day 1 | ±0.06 | --- |
| 12 hr evening, day 1 | ±0.11 | --- |
| 12 hr morning, day 2 | ±0.10 | --- |
| 12 hr evening, day 2 | ±0.05 | --- |
| 24 hr, day 1 | ±0.14 | 0.03 |
| 24 hr, day 2 | ±0.1 | 0.01 |

comparison of RTI prototype performance with the performance guideline specifications for hydrocarbon monitors is shown in Table 3.

TABLE 3. COMPARISON OF RTI GC-FID TO SOME SPECIFICATIONS IN EPA PERFORMANCE GUIDELINES (22)

| Performance Parameter | Units | Document Value | RTI Value |
|---|---|---|---|
| Range | ppm | 0-5 | Spec. met |
| Noise | ppm | 0.05 | 0.05 |
| Lower Detectable Limit | ppm | 0.1 | 0.1 |
| Interference Eq. | | | |
| Each Interferent | ppm | ±0.1 | not determined |
| Total Interferent | ppm | ±0.2 | |
| Zero Drift, 12- and 24-Hour | ppm | ±0.2 | ±0.11 |
| Span Drift, 24-Hour | percent | ±5 | ±2.8% maximum |
| Lag Time, Rise Time, Fall Time | minutes | 10 | within specs. |
| Precision | ppm | 0.3 | 0.09 |

## EFFECTS OF WATER VAPOR

The final step in the evaluation of the RTI prototype was the determination of the effects of water vapor on the response of the instrument. The equipment configuration for the test is shown in Figure 21. A cylinder of 1.99 ppm methane in HC free-air was connected to a bubbler fitted with a by-pass. The bubbler, enclosed in a heating mantle, was filled with distilled, deionized water. The bubbler outlet was connected to the GC by stainless steel tubing which was heated to 110°C by tape heaters; the GC oven was also held at 110°C. The dew point of the gas stream was measured at the inlet of the GC. The pressure at the GC inlet was also measured and maintained at $6.08 \times 10^4$ Pa (0.6 atm.) above ambient. This pressure was chosen to match the pressure in the sample and carrier lines, a condition which yielded minimum baseline disturbance when valve #1 was switched. The instrument was operated near the methane optimum, and seven injections were made at each dew point setting. The injections were made in THC mode so that the stripper column was by-passed. Peak area (by digital integration) and peak height were recorded for all samples. The initial injections with the bubbler by-passed gave the response of the "dry" methane, and the final set of injections, made with the bubbler by-passed again, assured that the instrumental response to the "dry" methane had not changed during the test. The data are presented in Table 4 where mean and standard deviation of both peak area and peak height are shown.

TABLE 4. DATA INDICATING WATER VAPOR INTERFERENCE OF RTI PROTOTYPE G.C.

| Sample | | Response | |
|---|---|---|---|
| Dew Point (°C) | % Water by Volume | Area[a] (Pulse Count) | Peak Height (mm) |
| 9 | 0.70 | 299285 ± 5050 | 79.8 ± 1 |
| 16 | 1.12 | 298826 ± 5700 | 77.9 ± 1 |
| 18 | 1.27 | 306232 ± 3650 | 81.7 ± 1 |
| 21 | 1.53 | 308740 ± 6352 | 82.4 ± 2.5 |
| 26 | 2.07 | 314789 ± 2764 | 81.9 ± 2 |
| 41 | 4.80 | 323803 ± 4040 | 85.0 ± 0.5 |
| 10 | 0.75 | 300065 ± 2219 | 82.7 ± 1 |
| Correlation ($R^2$)[b] | | 0.929 | 0.430 |

a. Mean value and standard deviation (N-1 weighting) of seven injections.

b. Correlation coefficients determined by two-variable linear regression analysis.

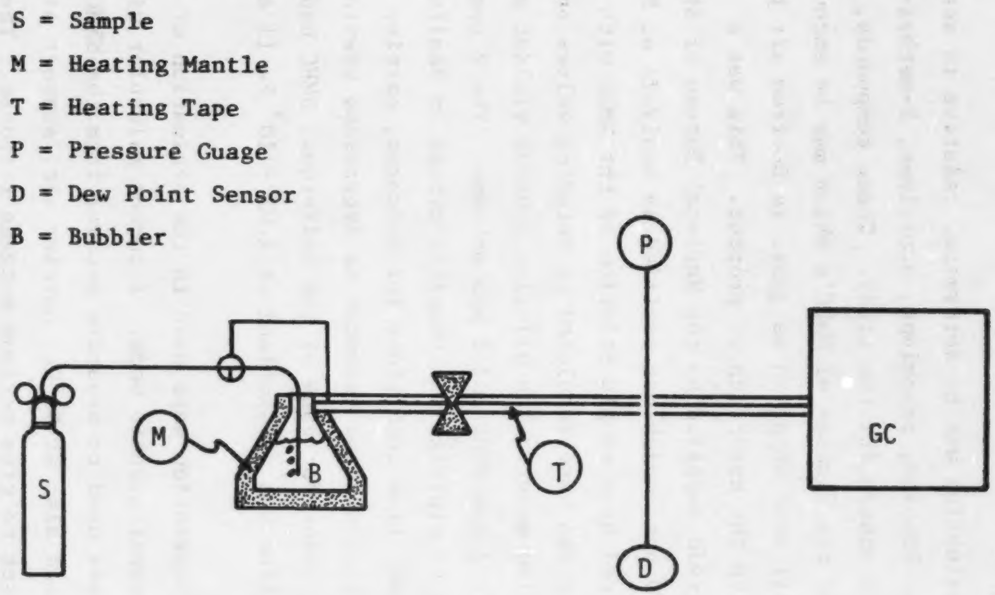
S = Sample
M = Heating Mantle
T = Heating Tape
P = Pressure Guage
D = Dew Point Sensor
B = Bubbler
P
GC
M
B
S
T
D

Figure 21. Experimental test setup.

The results are plotted in Figures 22 and 23 and can be summarized as follows:

1. As a function of sample dew point in the range of 9°C to 34°C (0.70% to 4.80% water vapor by volume), the peak area increased 6.8% with identical methane injections.
2. In the same range peak heights increased by 5%.
3. The goodness of linear fit was measured by the square of the correlation coefficient, $R^2$; peak area showed an $R^2 = 0.929$, and peak height showed an $R^2 = 0.430$.

INSTRUMENTAL RESPONSE TO NMHC

The next phase of the evaluation was to determine, relative to methane, the response to NMHC species. Propane, propylene, acetylene, 2-methyl-2-butene, toluene, and acetaldehyde were chosen for the study. These compounds, with methane, are representative of the classes of NMHC's which may be encountered in ambient air monitoring. All were supplied as gases in HC-free air by a commercial supplier (21) with the exception of propane. This was a Standard Reference Material grade supplied by the National Bureau of Standards with an analysis of 94.2 ± 0.9 ppm, which was verified by analysis at RTI. Sample gas streams were prepared by a single dilution of the NMHC with 2 ppm methane in HC free air. All flows were regulated by metering valves and were measured with a bubble flow meter. The dilution process yielded a sample stream of approximately 2 ppm NMHC and 2 ppm methane. The 2 ppm level for the NMHC was chosen to minimize the possible errors in dealing with low sample concentrations. Flow conditions for hydrogen, carrier air and support air were set for peak methane response as determined previously because the optimum operation point for each of the individual NMHC had not been determined. The sample line was pressurized at $1.01 \times 10^5$ Pa (1 atm.) above ambient.

Three different modes of operation were used in the evaluation of NMHC response. The first was a chromatographic mode. A carbon molecular sieve (20) column operated at 95°C was used to separate methane from the NMHC component. The FID was operated also at 95°C. Carrier air, support air, and hydrogen fuel flows were set to give maximum methane response. The second mode of operation was the strip-subtract method of the Federal Register (1). The stripper column was again a carbon molecular sieve, operated this time at 105°C to assure adequate backflushing prior to

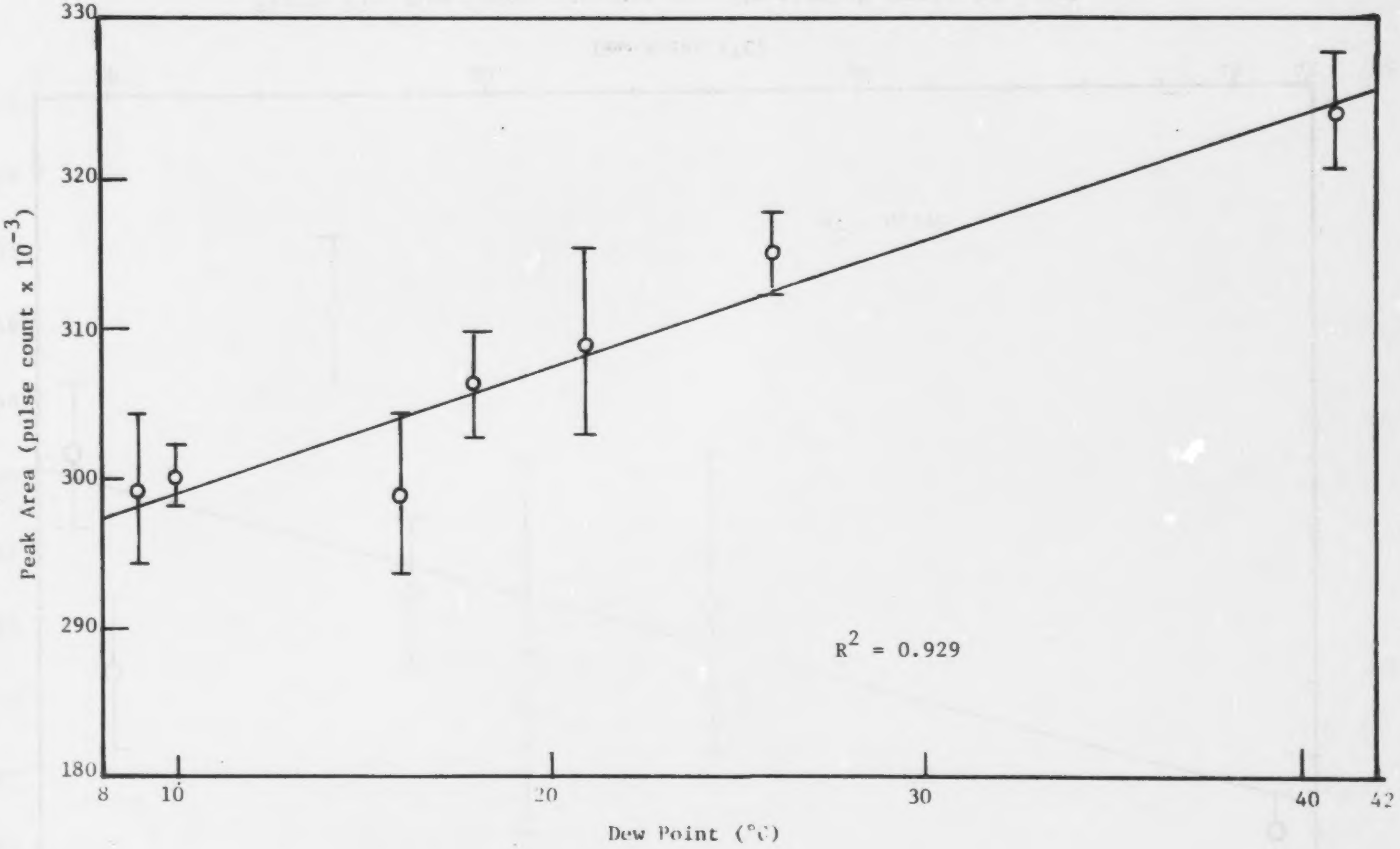

Figure 22. Peak area response as a function of sample dew point.

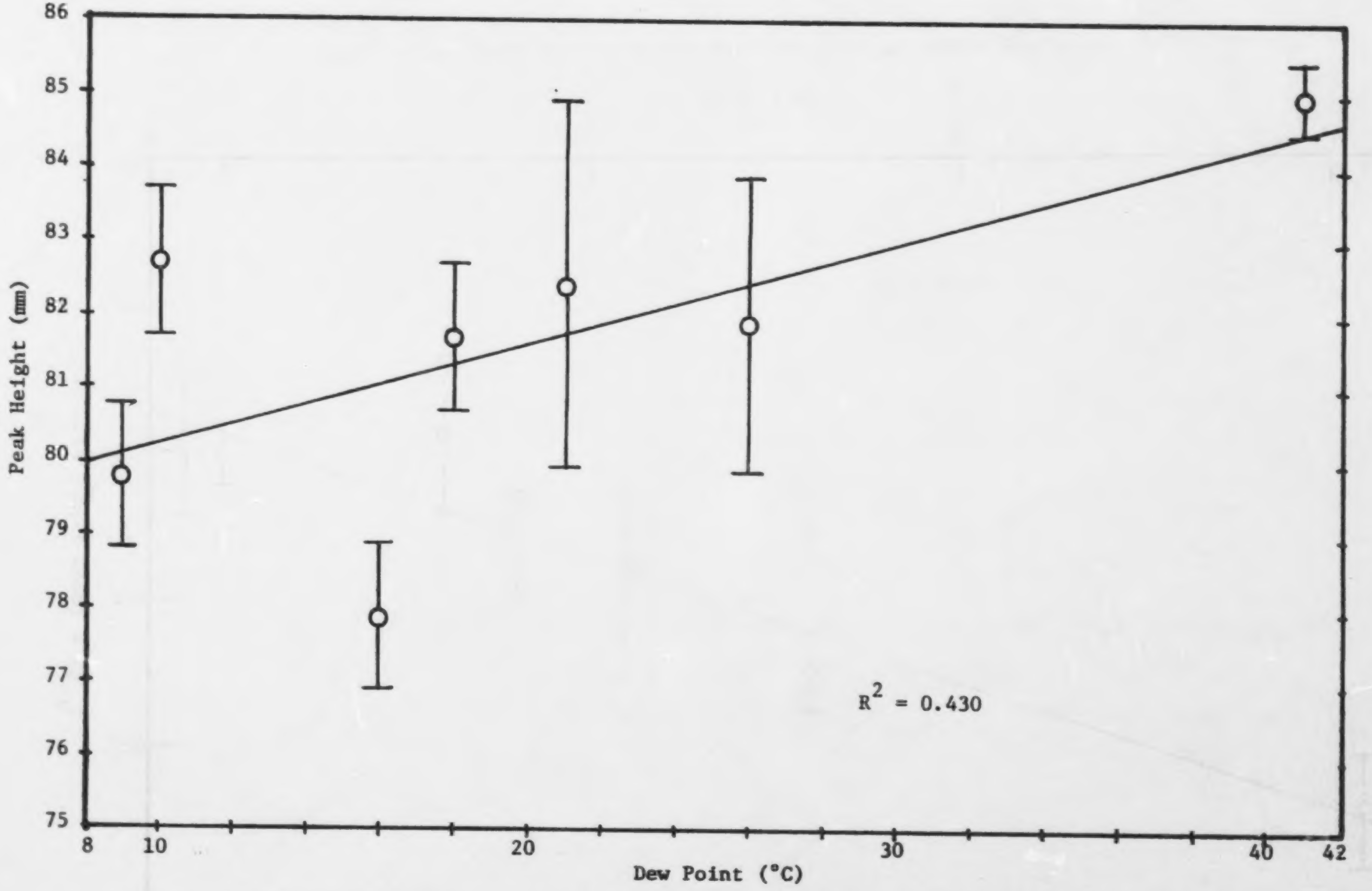

Figure 23. Peak height response as a function of sample dew point.

introduction of a new sample. The FID was also operated at 105°C. The same air and hydrogen flow rates were used as in the chromatographic mode. The third mode was the backflush method. In this mode methane was allowed to elute to the FID from the stripper column. Following this the NMHC is backflushed from the column into the FID for analysis. Again the carbon molecular sieve column was operated at 105°C as was the FID, with the same air and hydrogen flow rates. Because 2-methyl-2-butene and toluene were apparently partially retained on the carbon molecular sieve, these two compounds were re-run using 10% carbowax on a commercial support (20).

The results of these evaluations are shown in Table 5. The numbers which are presented are the effective carbon numbers (ECN) determined on a per-atom-of-carbon basis in the following manner:

$$ECN = \frac{R_{NMHC}}{C_{NMHC} \times N}$$

$R_{NMHC}$ is the concentration of NMHC's indicated by the instrument being used; $C_{NMHC}$ is the actual concentration; N is the number of carbon atoms per molecule. $R_{NMHC}$ calculation depended on which of the three mdoes of operation was being used; the chromatographic and backflush approaches yielded a direct value, but the strip method required subtraction of the methane component from the THC valve.

The ECN values for methane, propane, propylene, and acetylene are reasonably consistent with literature values as can be seen by examining the data from Ref. (23). Note however that careful attention must be paid to analysis conditions when making such comparisons. These conditions include, for example, sample pressure, sample flow rate, premixed- or diffusion-type flame systems, and fuel carrier ratio, to mention a few, and can significantly alter the ECN values for HC species.

The response of toluene and acetaldehyde was quite low, and the 2-methyl 2-butene response was marginal. Analysis of the toluene and 2-methyl-2-butene cylinders on a Perkin Elmer 900 GC showed that the concentration certified by the supplier (21) was correct; however, the acetaldehyde had degraded to 60% acetaldehyde and 40% acetic acid. One possible explanation is that there was some condensation and adsorption problem in the line connecting the gas mixtures to the RTI instrument. Toluene, 2-methyl-2-butene and acetaldehyde

TABLE 5. THE NMHC RESPONSE OF RTI INSTRUMENT IN VARIOUS MODES OF OPERATION ($CH_4$ = 1.0 AS BASIS)

| | Chromatographic | Strip | Backflush |
|---|---|---|---|
| Methane | 1.0 | 1.0 | 1.0 |
| Propane | 0.79 | 1.0 | 0.80 |
| Propylene | 0.70 | 0.75 | 0.50 |
| 2-Methyl-2-butene | 0.48 | 0.43 | 0.66(2) |
| Acetylene | 0.95 | 1.16 | 0.79 |
| Toluene | —(1) | 0.27 | 0.50(3) |
| Acetaldehyde | —(1) | 0.31 | —(4) |

(1) These compounds not eluted with carbon molecular sieve stripper column.

(2) This resulted from changing to 10% carbowax column; ECN = 0.52 with carbon molecular sieve.

(3) Resulted from changing to 10% carbowax column; ECN = 0.13 with carbon molecular sieve.

(4) Not tested in backflush mode.

Note: "Chromatographic" measurements were made with GC oven, containing column and FID, at 95°C. "Strip" and "Backflush" measurements were made at 105°C. Flow rates of hydrogen, carrier air and support air were maintained at the same levels for all three sets of measurements.

are normally liquid at room temperature and near one atmosphere pressure. The dilution and mixing system contained about 1.22 m (4 feet) of stainless steel tubing, 0.64 cm (0.25 inch) diameter, as well as a stainless steel mixing volume of 7.6 cm (3 inch) diameter and 10.2 cm (4 inch) length. This was all at room temperature. It is possible that some of the sample gas was "lost" in this system. However, there did not appear to be any induction period required to achieve steady state response to any of these compounds with the instrument. Furthermore, the same sample mixing system was used for the tests in all three modes of operation.

## SUMMARY OF RTI FID-GC EVALUATION

The prototype FID-GC exhibited a response to methane that was very similar to that for the FID alone. Response was independent of support air flow rate over the 100-300 $cm^3$/min range investigated. Response to methane peaked for both the hydrogen and carrier air flow rates. However, there is a peak in methane response versus the ratio of hydrogen to carrier air flow rate which differs slightly from the flow ratio using values of both hydrogen flow rate and carrier air flow rate which individually provide a peak response.

Response to methane increased linearly with inlet pressure at about 30% per atmosphere over the range of $1.15 \times 10^5$ Pa to $1.70 \times 10^5$ Pa. This is about one-third the increase expected on the basis of the ideal gas law and probably is due to the pressure drop through the sampling valve-sample loop path, which reduced the sample loop pressure below the inlet pressure.

Using synthetic carrier "air" of varying oxygen content, response to methane was found to vary only slightly with $O_2$ content above 20% $O_2$. However below about 19% $O_2$ FID response to methane decreased at about 10% per 1% change in oxygen content.

For the RTI instrument, the strip mode of operation was superior to the backflush mode. This result cannot be generalized, however, since it is a function of instrument design and column selection.

Based on the results of the evaluation, the RTI instrument was demonstrated to conform to the specifications of the EPA performance guidelines (22). Response to several different NMHC species varied, depending upon the method used to separate methane from the NMHC. Although it is well known that compound response is very sensitive to operating parameters [see Ref. 25, for example], ostensibly the same FID operating conditions were used. Slightly different temperatures were used, but the apparent ECN values for the condensible NMHC species appeared to be more dependent on column effects than anything else.

The effect of water vapor on response was somewhat surprising. The peak area and peak height increases which were noted on the RTI instrument are contrary to much of the literature (24). When comparing however, attention must be paid to experimental conditions. As an example, the presence of 1% of water has been reported to double the ionization-current in a pure hydrogen flame while retarding ionization by 30% in other flames (25). Definitive information on water vapor effects is not available for those engaged in making NMHC measurements and is a topic certainly worthy of further research, for water vapor will always be present in ambient sampling. It should be noted that the effects reported in this section were for water vapor carried directly into the FID with the sample. Presumably column effects such as site deactivation or displacement were not involved. One is directed to Section 7 of this report for further evidence of the impact of water vapor on ambient air monitoring.

Quite typically more humid atmospheric conditions are associated with lower atmospheric pressures. As reported in Section 4 the FID response changed on the order of 2% over the normal atmospheric pressure range. The pressure-induced deviation in response seems to operate in a direction which would augment the moisture-induced response increases. It appears possible to have an error source approaching 10% solely from normal atmospheric pressure and moisture variation, if it is assumed that all instruments respond as the RTI prototype.

It should be pointed out that this summary and the conclusions drawn from it are specific to the RTI design. The effect of the various operating parameters on response, however, are indicative of similar effects with other designs, although the quantitative measures would be expected to vary in detail with the particular design. The purpose of this phase of the evaluation is to illustrate that some operating parameters are more critical in their effect on response than others. This brings into question whether or not these critical parameters are known by the instrument designer and are sufficiently controlled over the operating life of the analyzer to maintain a stable response pattern. It also serves to illustrate to the users of these instruments that proper instrument set-up and maintenance are necessary to obtain good quality data.

# SECTION 6

# REVIEW OF COMMERCIAL INSTRUMENTS

Reviewing commercial instruments, particularly in a comparative manner, poses a fundamental problem because different instruments possess different operational philosophies and techniques. Basically, a nonmethane hydrocarbon analyzer (or total hydrocarbon analyzer) is composed of three separate subsystems: the pneumatics, the detector, and the signal processor. By partitioning the commercial analyzers in this manner, a comparison can be made which illustrates the operational nuances of a particular instrument, while not losing sight of the overall specifications prescribed by EPA. The purpose of this section is to analyze the design and fabrication of several common commercial analyzers, which were used in the side-by-side, comparative evaluation described in Section 7. The instruments compared are the following:

1. a Beckman 6800 Environmental Gas Chromatograph,
2. a Beckman 400 Total Hydrocarbon Analyzer,
3. a Bendix 8200 Environmental Gas Chromatograph,
4. a Bendix 8201 Hydrocarbon Analyzer, and
5. an MSA 11-2.

According to manufacturer's specifications, all these instruments meet the requirements for performing at least the total hydrocarbon measurement of the Federal Reference Method (1).

## DESIGN

For analysis these commercial instruments are partitioned into subsystems as follows. The pneumatics subsystem includes valving, tubing columns, flow and pressure controls, and, in general, all necessary hardware to transport a desired sample from the inlet port to the detector. The second subsystem is the detector. The only detector found in the instruments examined is the FID. The signal produced in the FID detector is conditioned and processed in an electronic subsystem. This subsystem also includes the control electronics for automatic operation of the analyzer in four of the six instruments evaluated.

## Pneumatics

The pneumatic design philosophy of commercial instruments appear to be divided into four categories.

Category I:

The simplest configuration is that of a total hydrocarbon analyzer, such as the Beckman 400 or Bendix 8400, which involves a minimum of hardware. Because this type instrument produces a continuous signal proportional only to the total hydrocarbon content of the sample, there are neither switching valves nor separation column; this instrument is incapable of separating methane from the non-methane component. The sample is typically pumped into the instrument, with sample pressure being controlled by a regulator and sample flow by a capillary. The fuel and burner air lines have pressure regulators and restrictors. It has been shown in the work with the RTI-designed instrument, and other studies (10,23,31), that the FID response varies dramatically with hydrogen and carrier flow rate, implying that the pressure drop across the restrictors must be sufficiently great to assure constant flow, and this appears to be a major requirement for stable operation.

Due to the simplicity of design, the operation of this category of instruments is usually not involved and the instrumental output is a single continuous trace on a strip chart recorder.

Category II:

The second category is a natural progression in increasing complexity and is capable of methane and non-methane determinations. A model representing this category is the MSA 11-2; it is a dual-FID, continuous-output instrument. The configuration is not unlike a parallel arrangement of two total hydrocarbon analyzers, in which one of the analyzers has been modified to respond to methane only. Again, the continuous output obviates the necessity for any type of switching valve. However, the use of two detectors requires that the sample stream be split and both flows be kept stable. The sample stream fraction to be used for a methane determination requires some type of column to either adsorb or catalytically burn all non-methane hydrocarbons. Pressure and flow regulation are accomplished by using pressure regulators and flow restrictors, as previously described, although the plumbing necessarily reflects the increase in complexity of the instrument.

With this design a new problem, column contamination, has been introduced. Columns which adsorb the non-methane constituent have a finite limit on the quantity of material which can be adsorbed, and a catalytic burner or cutter column, such as the MSA 11-2 employs, also must be periodically regenerated. Failure to perform necessary regeneration degrades column performance and impedes complete methane-non-methane separation leading to increasingly inaccurate measurements. Another possible problem is the degradation of column and catalytic surfaces by the gradual accumulation of water.

Category III:

The environmental chromatograph represents the next category. The level of complexity has increased significantly for several reasons. Characteristic instruments, as the Beckman 6800, Bendix 8200, and Bendix 8201, must separate the methane and non-methane fractions; this requires flow switching capability (usually at least two switching valves) and stripper and/or separation columns. There now is a timing requirement so that fractions are detected at the proper time. The introduction of switching valves adds more problems; these valves cannot switch instantaneously and may require several hundred milliseconds to switch. This finite time produces pressure surges which can seriously perturb the baseline; regardless of preventative measures, the instruments will usually reflect some of the switching induced pressure surge. Also, the seals in the switching valves can leak or seize and impair operation. An additional pressurized air supply is usually required to operate the valves.

The flow control is generally the same as previously described - regulators and restrictors - implying the continued need for large pressure drops across restrictors to maintain constant flow.

Category IV:

The final category represents instruments which operate in the "backflush" mode, meaning that a sample is injected onto a column which separates the methane, allowing it to pass on to the FID detector, and is then backflushed so that the non-methane component may be directed to the detector. These instruments, such as the Hewlett-Packard 5830A Gas Chromatograph or the Carle Series-R Analytical Gas Chromatographs, may have single or dual detectors and usually have only one switching valve. These instruments possess all the problems previously described plus one addition. The column obviously must give adequate resolution of NMHC and methane, and non-methane fraction must not adhere to the column material so tenaciously as to make removal overly difficult when backflushed. This can be accomplished with a multicomponent column packing.

In summary, most commercially available instruments, intended primarily for the use of total hydrocarbon or non-methane hydrocarbon measurement, fall into one of the four pneumatic design categories described. These categories are based on increasing instrument (and pneumatic) complexity, and it appears that the problems associated with each level of complexity are transmitted to higher levels.

## Detectors

All instruments examined in the comparative evaluation used flame ionization detectors. With the exception of the MSA 11-2 these were all essentially the same design - cylindrical collectors coaxial with the jet tip. The design advantages of this configuration were enumerated in Section 4 when the RTI prototype was discussed and will not be discussed further here. The FID used in the Beckman instruments is geometrically similar to the RTI design (see Fig. 6), with the bottom edge of the collector fitting down below the level of the jet tip. The FID used in the Hewlett-Packard Model 5830A is also similar. The Bendix FID differed only in that the cylindrical collector was raised slightly above the jet tip. The MSA 11-2 has an unusual geometry; the jet tip points horizontally and is coaxial with a Swagelok® ferrule (used as the collector), located about 3 mm (0.125 inch) from the jet tip. This geometry does not appear in the literature but is claimed by MSA to be less noisy. This design requires a lower polarization voltage for saturation (26).

The polarizing voltage in these instruments is typically applied to the jet, which is a good design feature, as was pointed out in Section 4. Beckman and Hewlett-Packard FID's employ positive jet potentials of about 100 volts. The Bendix instruments employ a negative voltage (-100v) on the jet tip. The MSA 11-2 polarizes with a positive potential which is much lower (15 volts) than the other instruments examined.

To summarize, the designs of the detectors are quite similar, except for that of MSA, which employs a unique geometry and a much lower polarizing potential on the jet than do the other designs.

## Electronics

The level of electronic complexity follows the level of pneumatic complexity. This is illustrated by the following descriptions.

1. The electronics of total hydrocarbon analyzers (Beckman 400, Bendix 8400) consist basically of an electrometer amplifier and an attenuator network to condition the continuous output signal for the strip chart recorders.

2. The MSA has essentially the same amplifier-attenuator configuration on each of its two continuously monitoring channels and includes an analog subtractor (difference amplifier) to give the non-methane response electronically ($THC-CH_4 = NMHC$).

3. The environmental chromatographs (Beckman 6800, Bendix 8200, Bendix 8201) use an amplifier-attenuator arrangement for continuous output but also have memory elements (sample-and-hold amplifiers) so that outputs can be transferred to recorders for operation in the bargraph mode when the appropriate timing signals are received.

4. The electronics of backflush instruments are essentially the same as described for the environmental gas chromatograph with the appropriate timing considerations for a methane and non-methane peak detection. However, because of the peak shape electronic integration is needed for peak quantification.

When discussing the electronics of these instruments, the crucial point is the manner in which the non-methane component is actually determined. The most prevalent method, the one prescribed in the Federal Register, requires subtraction of a methane determination from a total hydrocarbon determination. Since these numbers are typically of similar magnitude, any small errors in either result in large errors in their difference. Instruments in Category II and Category III use this method. An alternative approach is to make both the methane and non-methane measurement directly from a single sample injection by the backflush technique. This eliminates the necessity of subtracting two numbers of similar size.

A second important consideration is the method of quantification of detector signals. Peak area is recognized as generally the most accurate measure of concentration in batch analysis (27). Digital integration can be the most accurate manner of quantifying peak area (27). Use of digital data facilitates data manipulation and further has the advantage of being in the format used for reporting and comparison. Analogue integration is somewhat less accurate than digital integration but usually superior to peak height measurement, which is still frequently used for quantitation (28). In a study of the accuracy obtained from various methods, Gill (29) listed the following order for the precision of peak-area determintion, expressed in relative standard deviations.

1. planimetry, 4.0%;
2. triangulation, 4.0%;
3. height and width of half-height, 2.5%;
4. cutting and weighing, 1.7%;
5. disk integration, 1.3%;
6. electronic digital integrator, 0.4%.

Novák (30) has recently listed the conditions when peak height quantitative determinations are applicable:

1. narrow, tall peaks,
2. flow rate stability not possible, (e.g. temperature programming)
3. good peak symmetry, and
4. constant chromatographic conditions for a single material.

Of the instruments examined, none used digital integration. Peak height or signal level subtraction was used in all cases to make the quantitative evaluations in spite of the limitations imposed by conditions 3 and 4 of Novák's work.

## FABRICATION

In view of the significance of the comparative evaluation of the commercial instruments, careful examination of the fabrication of the instrument was necessary. The fabrication materials and details of an instrument can play a major role in determining instrument response and maintainability. This is particularly appropriate in the current discussion because the designs of all the analyzers appeared adequate to perform the non-methane measurement (keeping in mind that the subtraction of nearly equal magnitude measurement numbers has a large error potential constraining the instruments to very stable and reproducible operation for accurate results). What follows, then, is a summary and critique, instrument-by-instrument, of the fabrication. It should be noted that these evaluations are based on the examination of only one instrument of each model.

1. Beckman 6800

The materials of construction and layout of the Beckman 6800 exhibit good design practice. All sample lines, seals and valves are stainless steel, and the plumbing is accessible, allowing ease of maintenance and repair. The FID was clean, with neither jet tip nor collector showing undue oxidation. The temperature control by the oven was stable.

2. Beckman 400

Like the 6800, the construction of the Beckman 400 is good; the plumbing is stainless steel and accessible. This was the only instrument which used a battery for the polarizing voltage, but this presented no obvious problems, because of the low current.

3. MSA 11-2

The MSA 11-2 has several apparent materials problems. The sample line is made of copper, which has a tendency to adsorb oxygenated compounds and aromatics. This has been reported in the literature (Ref. 31, for example). The MSA also used plastic filter canisters and pressure regulators containing Buna-N rubber. The gas distribution block and selector valve are made of block aluminum although stainless steel shows better resistance to corrosion and is less likely to present compound adsorption problems. The geometry and fabrication of the FID made accurate positioning of the jet difficult. The instrument requires 3 liters/minute of sample which can be a large drain on cylinder supplies during calibration.

The instrument is designed and constructed so that repair and maintenance are easy to perform.

4. Bendix 8201

The fabrication of the 8201 is good; the flow lines are stainless steel, and plumbing is accessible and well-conceived. The jet tip and collector did show some oxidation, and one of the switching valves had to be replaced due to an O-ring breakdown.

5. Bendix 8200

The fabrication of the Bendix 8200 is also quite good. The plumbing was stainless steel and accessible. The jet and collector showed some oxidation. Plastic prefilters were used in the sample line.

It may be concluded, then, that the commercial instruments examined were all well made, and, with the possible exception of the copper sample line, the construction of these instruments should not be the limiting factor on their response characteristics. Copper sample lines can be a problem with certain classes of compounds; this fact was confirmed during the comparative evaluation with toluene and acetaldehyde. The plastic filters are a potential source of error, but their actual effect was not determined experimentally. Finally, many of the problems, such as jet collector oxidation, should be corrected during routine maintenance, and the valve problems, such as the ones experienced, are not uncommon or unreasonable.

## SELECTION OF OPERATING CONDITIONS AND CALIBRATION

Following evaluation of the RTI designed FID and gas chromatograph as described in Sections 4 and 5 of this report, a summary report was distributed to six manufacturers of analyzers for non-methane hydrocarbons along with questions about the selection of operating conditions and methods of calibration for their instruments. A list of individuals and firms contacted is given in Table 6. Response was generally good although one firm declined to send in answers to the questions posed. The questions are listed in Table 7. The answers were generally frank and it was apparent that a lot of thought had been given to the replies.

From the answers received the following information was drawn.

1. Selection of Flows. One manufacturer selects hydrogen and carrier gas flow settings to optimize response to methane, but pointed out that this does not insure peak response for other hydrocarbons. A second uses settings selected to optimize response to the greatest number of HC species. A third selects those flows that give a "stable, reproducible response" (presumably to all hydrocarbons). A fourth uses a carrier air flow that provides desired elution times from the analytical column. A fifth sets the $H_2$/carrier air ratio to prevent flame blowout from the air peak from the sample.

## TABLE 6. LIST OF MANUFACTURERS AND REPRESENTATIVES SURVEYED

Mr. John Scales
Sales Engineer
Bendix Process Instruments Division
P. O. Drawer 831
Lewisburg, WV 24901

Mr. D. W. Stevens
Market Development Manager
Analytical Instrumentation
Beckman Instruments, Inc.
2500 Harbor Boulevard
Fullerton, CA 92634

Mr. Pat Conner
Marketing Manager
Instruments and Systems Division
Meloy Laboratories, Inc.
6715 Electronic Drive
Springfield, VA 22151

Mr. Byron Behr
President
Byron Instruments, Inc
520 S. Harrington St.
Raleigh, NC 27601

Dr. Charles A. Burgett
Avondale Division
Hewlett-Packard
Route 41 and Starr Road
Avondale, PA 19311

Mr. William V. Dailey
Product Line Manager
Technical Products Division
Mine Safety Appliances Company
400 Penn Center Boulevard
Pittsburgh, PA 15235

## TABLE 7. LIST OF QUESTIONS IN SURVEY OF MANUFACTURERS

1. Do the operating instructions for initial pressure (and/or flow) settings for hydrogen and carrier gas for the FID's in your instruments insure operation at or near the peak of the response curve for the FID?
2. How were these settings determined, on a single prototype evaluation, a range based on randomly selected and tested production line units, individually for each instrument?
3. Are instrument specifications on drift, precision, etc., obtained from measurements on a single prototype, randomly selected and tested production line units, individual production unit testing?
4. How are precision and accuracy determined; i.e. what gases are used, are they analyzed and certified by supplier, are they spot checked (or exhaustively analyzed) by you, how many measurements are taken over what period?
5. Have you evaluated your instrument's response to non-methane hydrocarbons species by species?
6. Based on your experience (i.e., that of your field representatives), what do you consider to be the significant sources of error in each of the following aspects of the present Federal Reference Method for NMHC measurement:
    1. Instruments (and instrumental method)
    2. Reagents (operating and calibration gases)
    3. Procedure specified in the Federal Register
    4. Operator

   and can you suggest methods for minimizing these errors?

2. Method for Selection of Flows. One manufacturer chose settings based on a prototype design later modified somewhat "based on experience". A second used data from several prototypes, with these initial parameters based on prior experience. A third uses "research data and evaluation of randomly selected units". A fourth adjusts settings based on tests on prototypes, pilot runs and production units. A fifth individually adjusts settings for each instrument produced (with criteria not specified.)
3. Basis for Specifications. For all manufacturers noise, span and zero drift are checked for each instrument produced prior to delivery. Precision is checked on random instruments by one manufacturer. The others check each instrument, over time spans that vary. (See answers to question 4, below). Accuracy checks were qualified by statements that reduced to "the accuracy check depends upon the accuracy of the determination of the calibration gas used."
4. Calibration Gases and Methods. Three of the manufacturers depended on certified analysis by gas supplier. One, who uses diluted gases, has experienced several cases where the certified analysis was substantially in error. Consequently, this manufacturer uses an intercomparison technique to identify gross errors. This manufacturer's zero, noise, span and precision checks are made over a 24 hour period. A second manufacturer cited similar problems with "certified analyses" and also uses an intercomparison technique to check for reproducibility. This manufacturer checks over a 48 hour period. Another manufacturer blends gases in-house and analyzes to about 1% accuracy at 5 ppm level. Their instrument calibration stability checks are made over an 8 hour period. No data on the time period of the calibration stability tests were given by the other two manufacturers.
5. Non-Methane Hydrocarbon Response. Three out of five manufacturers responding have done little or no species-by-species evaluation of NMHC response of their instruments. Another manufacturer has performed extensive species by species tests and reported agreement to within 12% of literature values, except for toluene where wall adsorption was a problem.

6. Problems with Present Federal Reference Method. The responses were generally organized by the categories of instrument, reagents, procedure and operators. These are summarized as follows:

   a) Design and construction difference probably introduce significant differences in species by species NMHC response as well as linearity of response. Three out of five respondents thought that the present Reference Method should be revised to include design options other than the present strip/subtract technique.

   b) Calibration gases were uniformly highlighted as a problem due to contamination and/or inaccurate analysis by the gas supplier. Another problem cited was the instability of low ppm gas mixtures.

   c) One respondent cited the need for more specificity of reagents and calibration gases. Two explicitly stated that the procedure was too restrictive with respect to the instrumental method specified.

   d) All respondents agreed that more operator training was necessary, citing the relative sophistication of the instruments contrasted with the (usual) inexperience of operators and maintenance personnel.

Along with these critiques of the present method there were several recommendations for changes, which will be cited in the discussion of Section 8 of this report.

This review of commercial instruments provides the background for the next section, which reports a side-by-side comparative evaluation of several of the instruments performed to determine the significant source(s) of discrepancy in field measurements of non-methane hydrocarbons.

# SECTION 7

## COMPARATIVE EVALUATION

Following the evaluation of the RTI designed FID-GC instrument reported in Sections 4 and 5, this instrument was prepared along with five commercial analyzers, for a side-by-side comparative evaluation in order to determine relative performance with regard to

1. calibration stability,
2. non-methane hydrocarbon response, and
3. operational characteristics.

This section describes the test arrangements and procedures and analyzes the data obtained. Detailed test data are given in Appendix B.

### TEST ARRANGEMENTS

A list of the instruments used in the comparative evaluation is given in Table 8. Instruments were located side-by-side in the same laboratory and were subjected to the same diurnal temperature variation (about 22° to 28°C). Sample gases were introduced to a common manifold which permitted simultaneous samples to be drawn by each of the instruments under test. The flow arrangements are shown schematically in Figure 24. Commercial analyzers were placed into operation in strict accord with the manufacturer's instructions.

The list of reagent gases and concentration levels for the evaluation are shown in Table 9. The hydrocarbon stock mixtures were those shown in Table 10, which gives the gas supplier's analysis and the RTI analysis. The latter were carried out on a Perkin-Elmer Model 900 gas chromatograph. This instrument was also used to determine the total hydrocarbon content of the air and the hydrogen fuel for the FID. The air was obtained from a catalytic cleanup system-nickel oxide on firebrick operated at 450°C. This supply was monitored periodically during the test sequence with the highest THC concentration measured at less than 50 ppb. The THC content of the hydrogen was less than 100 ppb.

TABLE 8. INSTRUMENTS USED IN COMPARATIVE EVALUATION

a. Instruments provided by EPA

| EPA No. | Serial No. | Instrument |
|---|---|---|
| 083170 | 33082 | Analyzer, Bendix Reactive Hydrocarbon, Model 8201 |
| 102671 | 2014 | Analyzer, MSA Non-Methane Hydrocarbon, Model 11-2 |
| 090653 | 28713 | Analyzer, Gas Chromatograph, Bendix, Model 8200 |
| 083182 | 1001018 | Analyzer, Total Hydrocarbon, Beckman Model 400 |

b. Instrument provided by RTI

| RTI No. | Serial No. | Instrument |
|---|---|---|
|  | 1000389 | Analyzer, Gas Chromatograph, Beckman Model 6800 |
| ---- | --- | Analyzer, Prototype Hydrocarbon |

## TABLE 9. LIST OF REAGENT GASES AND $CH_4$/NMHC MIXTURES FOR COMPARATIVE EVALUATION

**Zero air:** <50 ppb THC

**Hydrogen:** <100 ppb THC

**Span gas (80%):** 8 ppm $CH_4$ + <0.05 ppm NMHC

**Span gas (20%):** 2 ppm $CH_4$ + <0.05 ppm NMHC

| Mixes: | Methane Background | |
|---|---|---|
| | 2 ppm $CH_4$ | 8 ppm $CH_4$ |
| Propane<br>($C_3H_8$) | 0.10<br>0.25<br>0.50<br>1.00<br>2.00 | 0.1<br>0.25<br>0.50 |
| Propylene<br>($C_3H_6$) | 0.25<br>0.50<br>2.00 | 0.25<br>0.50<br>2.00 |
| Acetylene<br>($C_2H_2$) | 0.25<br>2.00 | 0.25<br>2.00 |
| Ethylene<br>($C_2H_4$) | 0.25<br>2.00 | 0.25<br>2.00 |
| Toluene<br>($C_7H_8$) | 0.25<br>2.00 | 0.25<br>2.00 |
| Acetaldehyde<br>($CH_3CHO$) | 0.25<br>2.00 | 0.25<br>2.00 |

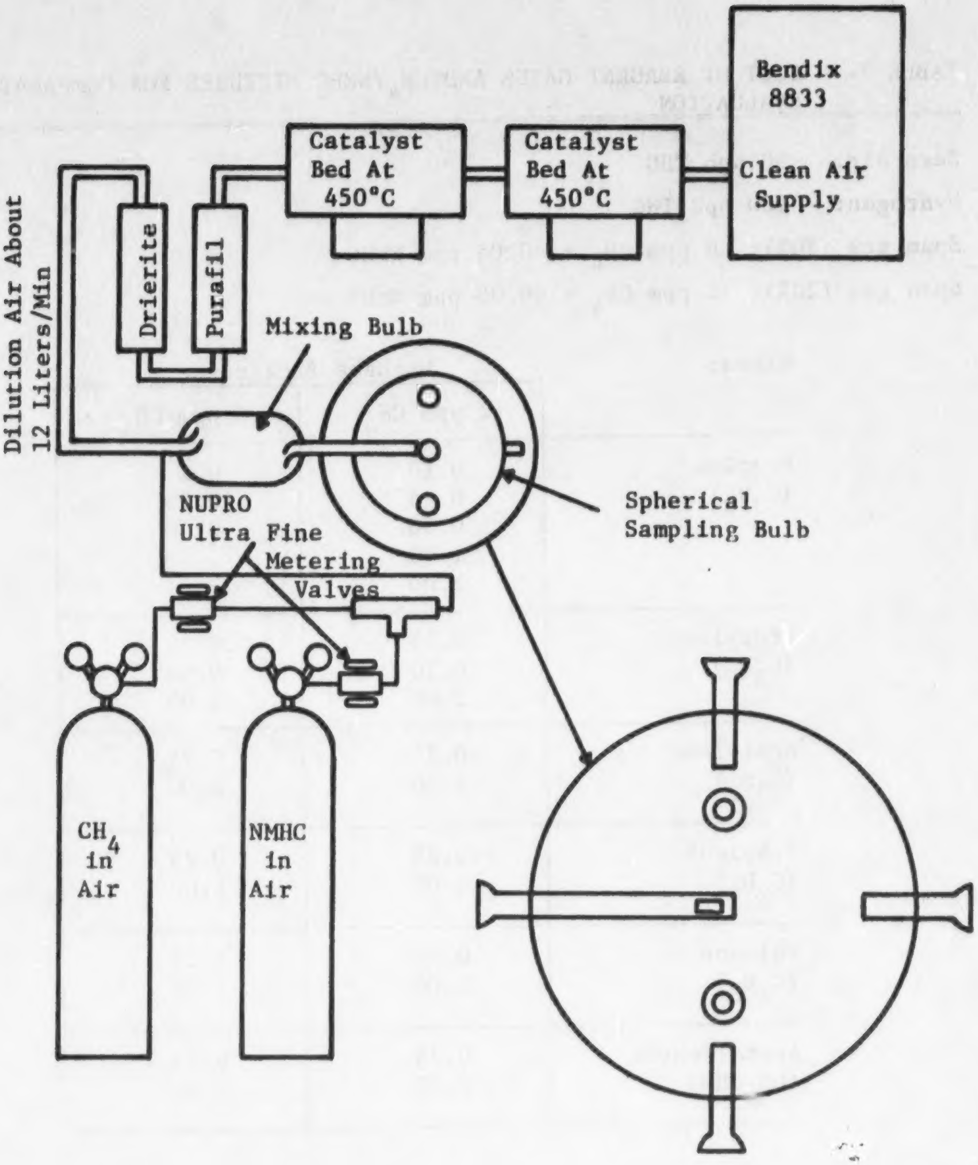
Bendix
8833
Catalyst
Bed At
450°C
Catalyst
Bed At
450°C
Clean Air
Supply
Dilution Air About
12 Liters/Min
Drierite
Purafil
Mixing Bulb
NUPRO
Ultra Fine
Metering
Valves
Spherical
Sampling Bulb
CH4
in
Air
NMHC
in
Air

Figure 24. Schematic diagram of flow system used for comparative evaluations.

TABLE 10. LIST OF STOCK HYDROCARBON/AIR REAGENTS WITH REPORTED AND MEASURED CONCENTRATIONS

| Compd. | Source | Supplier's Reported Conc. (ppm) | RTI[1] (ppm) |
|---|---|---|---|
| $C_3H_8$ | NBS | 94.2 ± 0.9 | 95 ± 0.7% |
| $C_3H_6$ | Scott | 205 ± 2% | 205 ± 3.0% |
| $C_2H_2$ | Scott | 203 ± 2% | 203[3] |
| $C_7H_8$ | Scott | 198 ± 2% | 206 ± 3.0% |
| $C_2H_4$ | In-house blend | ---- | 260.1 ± 4.5% |
| $CH_4$ #1 | In-house blend | ---- | 152.36 ± 2.0% |
| $CH_4$ #2 | In-house blend | ---- | 152.62 ± 3.0% |
| $CH_3CHO$ | Scott | 183 ± 2% | ----[2] |

---

[1] All RTI analyses performed on a Perkin-Elmer Model 900 Gas Chromatograph.

[2] Acetaldehyde had oxidized to approximately 60% - $CH_3CHO$
40% - $CH_3\ CO_2H$.

[3] Single gas chromatographic analysis.

The concentration levels of hydrocarbons in Table 9 were obtained by precision flow blending of stock hydrocarbon/air mixtures with the catalytically purified air. Flows were measured at least twice per day to assure that the desired hydrocarbon levels were being maintained. Daily flow variations were typically less than 1%; only one day showed a large variation (10%) and the sample concentrations were recalculated accordingly.

## TEST PROCEDURE

During the first part of the evaluation, which started July 28, 1976, the instruments were examined for calibration stability. Instrument zero points and spans were set with hydrocarbon free (<50 ppb) air and with 8 ppm methane in air, respectively. All instruments were operated on a 10 ppm full scale range throughout the entire test. The bargraph response mode was used for the Beckman 6800, Bendix 8200 and Bendix 8201. The Beckman 400 and MSA 11-2 gave a continuous signal. Zero and span stabilities over a twenty day period were monitored. No instrumental adjustments were made unless absolutely required for analyzer operation (for example, relighting an extinguished flame.) All such adjustments were logged.

In addition to zero and span stability, precision was ascertained during this period by repetitive alternate injections of 2.2 ppm $CH_4$ and 0.53 ppm propylene plus 2.2 ppm $CH_4$.

The second phase of the evaluation utilized varying levels of non-methane hydrocarbons, on a species-by-species basis, with and without a $CH_4$ background as shown in Table 9. When a methane background was used, it was at either a 2 ppm or an 8 ppm level. The purpose of this was to determine the effective carbon number (ECN) response of each instrument on a species-by-species basis and to determine whether or not any synergistic effects could be detected. Also during this test phase the linearity of response was determined using propane.

The final phase was a 3-day sampling of ambient air in the Research Triangle Park, N. C., conducted over the period of August 28 to August 31, 1976.

Throughout the entire evaluation all instruments were operated from a common source of hydrogen fuel and from a common air supply for both the carrier and FID support air. This was done to insure that all instruments had the same bias (if any) due to reagent gases.

## OPERATIONAL SUMMARY

During the testing sequence various observations were made about the operating characteristics and maintenance problems which were experienced. These are summarized below for each instrument.

### Bendix 8201

This instrument flamed out 7/29/76 and a very difficult time was experienced trying to get the instrument reignited. A Bendix representative accomplished this 7/30/76. An O-ring on one of sampling valves began leaking 8/15/76. This had to be replaced and flows readjusted (8/17/76), after which the instrument worked well. During the NMHC response evaluations the instrument did not respond to acetaldehyde. Careful setting of backflush air was necessary to keep an unperturbed baseline when the stripper column was backflushed.

### MSA 11-2

This instrument had several flame outs during the early part of first test phase due to pressure transients on the common reagent supply lines. These occurred whenever another instrument was being connected or disconnected. This was a unique phenomena for the test setup and would not be expected in normal operation. Trouble was experienced with the cutter oven beginning July 30, and there was evidence of incomplete non-methane oxidation until August 2, which resulted in an apparently low response for propane (due to the higher output of the methane channel) until this date. This problem was rectified and the cutter oven temperature control worked properly during rest of test, resulting in ECN values comparable to those of the other instruments.

Effects of sample line copper tubing (see discussion of Fabrication in Section 6) were noted with toluene and acetaldehyde. Both gave a time lag response, described by the following approximate equations, which were determined graphically,

$$\text{Toluene:}\quad C = C_o\ (1 - e^{-t}/7.55) \qquad (9)$$

$$CH_3CHO:\quad C = C_o\ (1 - e^{-t}/7.60) \qquad (10)$$

where t is in minutes elapsed, following a step change in concentration, and $C_o$ is the concentration step magnitude for the space in ppm. These long time constants, about 7.5 minutes, implied that rapid concentration changes might go unnoticed, or be attenuated.

## Beckman 6800

Trouble was experienced with the slider in the $CH_4$-CO sampling valve. It would stick in mid-position. This valve was replaced, and the 6800 worked well afterwards. Also the instrument had a defective Auto-Manual switch. There appeared to be some trouble with electronics, with occasional irregular peaks and spikes noted. As with the MSA 11-2 some flame outs occurred when work on other equipment affected line pressures. As pointed out before, however, this was a problem unique to this experimental set up.

The sticking valve resulted in the loss of some of the data from the long-term stability test.

## Beckman 400

The only real problem experienced was an occasional noisy signal, the cause of which was never identified. As with other instruments in the test there was an occasional flame out when one of the other instruments was put on-line or taken off-line, due to reagent gas pressure fluctuations.

## Bendix 8200

No operational problems were experienced with this instrument. It displayed good stability and reliable performance.

## RTI Prototype

Some flame outs occurred due to reagent gas pressure fluctuations when work being performed on other instruments affected line pressure. A solenoid valve failed in the air switch which operated the sample valve. A hand operated system was fabricated and used for the remainder of the test. The baseline showed some downward drift due presumably to hydrogen or carrier flow fluctuation toward the end of the stability test.

## DATA ANALYSIS

The electrical output signal from each instrument was fed to separate strip chart recorders. Details on these recorders are presented in Appendix C which reports on evaluation to determine the calibration stability and dynamic characteristics of these components of the measurement systems. It was concluded that these components contributed negligible error to the overall measurement.

Whenever trouble was experienced with an instrument due to equipment malfunction or being temporarily decommissioned, such as by FID flame-out due to a common supply line pressure surge, the data from the instrument was discarded until proper operation was again attained.

Zero and span drift were obtained by taking hourly data from each chart and calculating the mean and standard deviation for each day. These are plotted and presented, along with other test data, in Appendix B.

Precision for $CH_4$ (at 2.2 ppm) and THC (0.53 ppm) propylene/2.2 ppm $CH_4$) were calculated as twice the standard deviation of successive repetitive measurements of these input samples over a period of 13 days. It should be noted that some instruments were inoperative during this period. Only operating days were used to calculate precision for these instruments.

The ECN values were calculated on a per-atom-carbon basis, as was done in Section 5. The ECN's which are reported represent averages of all the ECN's for a particular NMHC. These data were further broken down into ECN's determined with a methane background and when only the NMHC was being sampled; the differences in these ECN values are reported. Also reported are "corrected" ECN's which were obtained by multiplying the "normal" ECN, determined on a $CH_4 = 1.0$ basis, by the reciprocal of the propane ECN for the instrument upon which the particular determination was made. Methane yielded a higher response than NMHC on a per carbon atom basis in all of the instruments evaluated, and the "corrected" ECN is an effort to compensate for this.

Another important feature of the NMHC data illustrates the need for frequent (daily or more often) calibration even though calibration frequency is not presently specified in the Reference Method (1). To develop this two methods of data reduction are used. The first method uses response determined by a single 80% span calibration performed at the beginning of the 14-day NMHC test period. These data necessarily reflect all the span and zero drifts which occurred during the test period.

The second method takes advantage of the fact that the injection sequence for a typical NMHC was begun with $CH_4$ only, followed by $CH_4$/NMHC mixture, and terminated with the NMHC only. This sampling sequence gave the effect of a daily (or more often, in some cases) span calibration either at the 20% or 80% span level. The differences due to data reduction based on the two different methods were found to be significant, as will be discussed later.

For the ambient air measurements the initial calibration prior to the start of the three day test was used for data reduction.

## RESULTS AND DISCUSSION

From the data analysis procedure described in the previous section the following results are obtained.

### Zero Drift

Table 11 shows the zero drift of each instrument reported in three categories. The first column gives the % of operating days when the ±0.2 ppm 24-hour zero drift specification of the EPA performance guidelines (22) was not met. The second column gives the % of operating morning hours (0000-1200) when the ±0.2 ppm 12-hour specification was not met. The third column gives the % of operating afternoon-evening hours (1200-2400) when the ±0.2 ppm 12-hour specification was not met. Instruments with both a methane channel and a THC channel have two entries per column. The first is for the $CH_4$ channel response to zero air, and the second is for the THC channel response to zero air.

As discussed in the OPERATIONAL SUMMARY the Beckman 6800 instrument had a faulty $CH_4$-CO sampling valve during the initial test phase. This is believed to be the cause for the excessive deviations of zero drift shown; the sticking valve altered the $H_2$ carrier flow rate thereby altering the flame conditions and output levels.

TABLE 11. ZERO DRIFT PERFORMANCE OF INSTRUMENTS

| | % of Operating Days when ±0.2 ppm 24-Hour Zero Drift Spec. was Not Met | % of Operational Morning Hours (0000-1200) when ±0.2 ppm 12-Hour, Zero Drift Spec. Not Met | % of Operational Afternoon Hours (1200-2400) when ±0.2 ppm 12-Hour, Zero Drift Spec. Not Met |
|---|---|---|---|
| Bendix | 0,0 | 0,0 | 0,0 |
| Bendix 8201 | 6,6 | 0,0 | 0,0 |
| Beckman 400 | 21 | 16 | 21 |
| Beckman 6800 | 31,25 | 41,47 | 47,35 |
| MSA 11-2 | 12,0 | 0,0 | 0,6 |
| RTI | 23 | 0 | 8 |

Note: When two numbers appear, the first refers to $CH_4$ determinations of zero air and the second to THC determinations of zero air.

Note: See note on Table 12 concerning Beckman 6800 data.

## Span Drift

Table 12 shows the span drift of the instrument reported as the percentage of operating days when the span drift did not meet the EPA performance guideline standard of ±5% (22). All instruments exceeded the specification a significant fraction of the time.

TABLE 12. SPAN DRIFT PERFORMANCE OF INSTRUMENTS

Span Drift - % of long term stability test when instrument did not meet 24-hour span drift requirement

Bendix 8200 - 2/13 × 100 = 15.4%
Bendix 8201 - 3/12 × 100 = 25%
Beckman 400 - 9/13 × 100 = 69.2%
Beckman 6800 - 7/10 × 100 = 70%
MSA 11-2 - 6/13 × 100 = 46.2%
RTI - 2/7 × 100 = 28.6%

Note: Beckman 6800 met all zero and span drift requirement during first 3 days of test when valve was functioning properly. Data included solely to illustrate effect of valve failure.

## Precision

The precision of the instruments is shown in Table 13. These values should be compared to the EPA performance guideline specification of 0.3 ppm (22). The precision on both the methane channel (measured at 2.2 ppm $CH_4$) and the total hydrocarbon channel (measured at 0.53 ppm propylene plus 2.2 ppm $CH_4$) is reported. All instruments were within this specification.

TABLE 13. PRECISION OF INSTRUMENTS ON METHANE AND TOTAL HYDROCARBONS CHANNELS

| | $CH_4$ (ppm) | THC (ppm) |
|---|---|---|
| Bendix 8200 | 0.05 | 0.04 |
| Bendix 8201 | 0.04 | 0.06 |
| Beckman 400 | ---- | 0.20 |
| Beckman 6800 | 0.03 | 0.03 |
| MSA 11-2 | 0.05 | 0.10 |
| RTI | 0.11 | 0.16 |

## Linearity

Propane was used to determine NMHC response linearity over the concentration range 0.1 ppm to 2.0 ppm. Data for five of the six instruments are reported in Figure 25. All of the instruments responses appeared linear in this range; however, insufficient data were collected to determine accuracy and precision in the test range. The fact that a 1 ppm sample of propane, for example, does not yield an equivalent 3 ppm $CH_4$ response, reflects the less efficient ionization or ion collection of propane.

## Non-Methane Hydrocarbon Response

Two methods were used to analyze the data from this part of the evaluation. The first method was to use the 80% span calibration response to methane, obtained at the start of the 14 day test phase as the basis for determining the response of each instrument to the various NMHC species. The resulting data is presented in Tables 14-17. This data will not be discussed in detail except to point out the much larger discrepancies in response to the different NMHC species, both on an intra-instrument and inter-instrument basis, which appear due to the shifting calibration of each instrument over the test period.

The second method of data reduction was to use the daily calibration provided by single injections of either 20% of span methane concentration or 80% of span methane concentration, as the basis. This data is presented in Tables 18-21. Because of the more frequent calibration it is believed to be more representative of instrument response characteristics and will be discussed in detail.

In Table 18 the ECN values are shown using a methane ECN = 1.0 basis. The response of acetaldehyde was by far the lowest with a NMHC average of 0.39 (20% lower than $C_2H_4$, the next lowest), omitting the Bendix 8201 which did not respond. The MSA exhibited almost three times the response of the Beckman 400 and 6800 and the Bendix 8200 and about 70% larger response than the RTI instrument. However it did take the MSA a considerable length of time to reach this response level. Regardless of the exact nature of the poor response, the clear implication is that accurate $CH_3CHO$ determinations would be difficult with the instruments used in the comparative evaluation in a reasonable time frame. Because of the low ECN, $CH_3CHO$ data was not included in the rest of the analysis.

Important information on the uniformity of NMHC response is found in Table 18 in the row which lists the mean of the NMHC response for each instrument and the column which lists the average for each of the NMHC species for the instruments used in the study. The average value for the NMHC's ranged

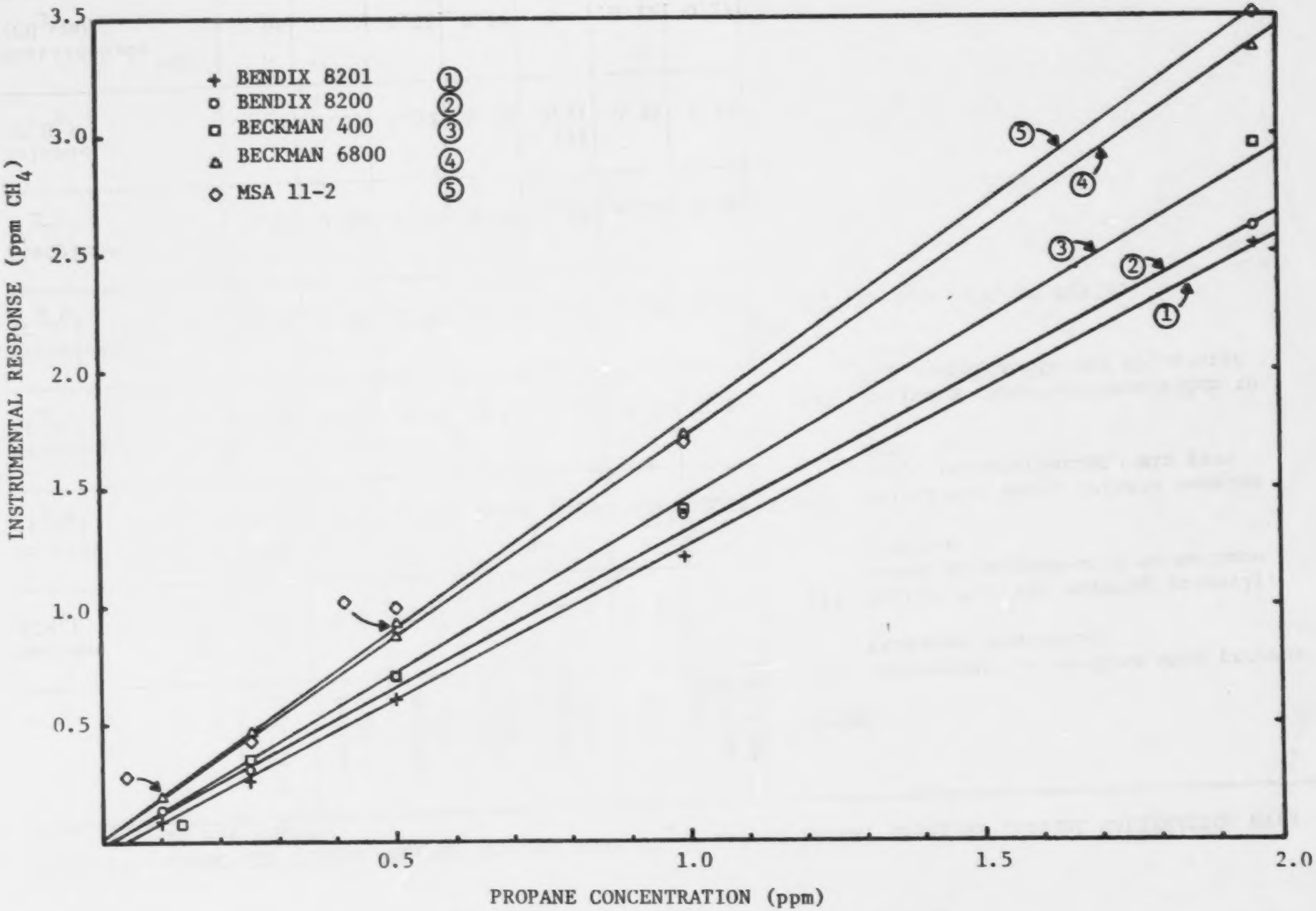

Figure 25. Linearity of propane response.

TABLE 14. EFFECTIVE CARBON NUMBERS OF NMHC WITH $CH_4$ = 1.0 AS BASIS, APPLYING INITIAL CALIBRATION OVER 14 DAY PERIOD

| | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 | RTI | NMHC Species Average |
|---|---|---|---|---|---|---|---|
| Methane ($CH_4$) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Propane ($C_3H_8$) | (2)<br>0.64 | 0.48 | 0.60 | 0.46 | 0.38 | —(1) | 0.51 |
| Ethylene ($C_2H_4$) | 0.48 | 0.25 | 0.42 | 0.32 | 0.38 | 0.34 | 0.37 |
| Propylene ($C_3H_6$) | 0.76 | 0.31 | 0.58 | 0.32 | 0.32 | 0.39 | 0.45 |
| Acetylene ($C_2H_2$) | 0.55 | 0.34 | 0.56 | 0.60 | 0.47 | 0.24 | 0.46 |
| Toluene ($C_7H_8$) | 0.77 | 0.25 | 0.52 | 0.39 | (3)<br>0.31 | 0.35 | 0.43 |
| Acetaldehyde(4) ($CH_3CHO$) | 0.66 | 0.12 | 0.52 | 0.20 | 0 | 0.12 | 0.27 |
| Mean of NMHC(5) per instrument | 0.64 | 0.33 | 0.54 | 0.42 | 0.37 | 0.36 | 0.44 |

Notes:

(1) Instrument not on-line when propane response determined.

(2) Cutter oven not working properly; based on propane-with-no-methane samples.

(3) Calculated using toluene samples only; toluene/methane mix gave ECN = 0.1.

(4) Analysis showed decomposition to 60% acetaldehyde and 40% acetic acid.

(5) Excludes $CH_3CHO$ ECN's.

TABLE 15. RESULTS OF CORRECTING NMHC RESPONSE TO PROPANE, APPLYING INITIAL CALIBRATION OVER 14 DAY PERIOD

| | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 | RTI |
|---|---|---|---|---|---|---|
| Methane ($CH_4$) | 1.56 | 2.08 | 1.67 | 2.17 | 2.63 | 2.86 |
| Propane ($C_3H_8$) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | (1)<br>--- |
| Ethylene ($C_2H_4$) | 0.75 | 0.52 | 0.70 | 0.70 | 1.0 | 0.97 |
| Propylene ($C_3H_6$) | 1.19 | 0.65 | 0.97 | 0.70 | 0.84 | 1.11 |
| Acetylene ($C_2H_2$) | 0.86 | 0.71 | 0.93 | 1.30 | 1.23 | 0.69 |
| Toluene ($C_7H_8$) | 1.20 | 0.52 | 0.87 | 0.85 | 0.82 | 1.0 |
| Acetaldehyde ($CH_3CHO$) | 1.03 | 0.25 | 0.87 | 0.43 | 0 | 0.94 |
| Mean of NMHC | 1.0 | 0.68 | 0.89 | 0.91 | 0.98 | 0.34 |

Notes:

(1) Use toluene ECN = 1.0

(2) Notes from Table 14 apply.

(3) Method of Calculating Table 15:

$$R = \frac{\text{ECN of NMHC from Table 14}}{\text{ECN of } C_3H_8 \text{ for that Instrument}}$$

## TABLE 16. EFFECT OF METHANE ON ECN OF NMHC, APPLYING INITIAL CALIBRATION OVER 14 DAY PERIOD

| | | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 | RTI |
|---|---|---|---|---|---|---|---|
| Propane ($C_3H_8$ | With $CH_4$ | — | 0.40 | 0.56 | 0.52 | 0.54 | --- |
| | No $CH_4$ | 0.64 | 0.48 | 0.60 | 0.46 | 0.38 | --- |
| Ethylene ($C_2H_4$) | With $CH_4$ | 0.64 | 0.58 | 0.47 | 0.37 | 0.37 | 0.42 |
| | No $CH_4$ | 0.48 | 0.25 | 0.42 | 0.39 | 0.38 | 0.34 |
| Propylene ($C_3H_6$) | With $CH_4$ | 0.73 | 0.45 | 0.52 | 0.39 | 0.35 | 0.46 |
| | No $CH_4$ | 0.76 | 0.31 | 0.58 | 0.32 | 0.32 | 0.39 |
| Acetylene ($C_2H_2$) | With $CH_4$ | 0.64 | 0.70 | 0.67 | 0.67 | 0.50 | 0.51 |
| | No $CH_4$ | 0.55 | 0.34 | 0.56 | 0.60 | 0.47 | 0.24 |
| Toluene ($C_7H_8$) | With $CH_4$ | 0.87 | 0.49 | 0.54 | 0.49 | --- | 0.50 |
| | No $CH_4$ | 0.77 | 0.25 | 0.52 | 0.39 | 0.31 | 0.35 |

Note: See notes on Table 14.

TABLE 17. RATIO OF $\frac{\text{ECN (NO CH}_4\text{)}}{\text{ECN (WITH CH}_4\text{)}}$, APPLYING INITIAL CALIBRATION OVER 14 DAY PERIOD

| | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 | RTI |
|---|---|---|---|---|---|---|
| Propane ($C_3H_8$) | — | 1.20 | 1.07 | 0.88 | 0.70 | — |
| Ethylene ($C_2H_4$) | 0.75 | 0.43 | 0.89 | 1.05 | 1.03 | 0.81 |
| Propylene ($C_3H_6$) | 1.04 | 0.69 | 1.12 | 0.82 | 1.09 | 0.85 |
| Acetylene ($C_2H_2$) | 0.86 | 0.49 | 0.84 | 0.90 | 0.94 | 0.47 |
| Toluene ($C_7H_8$) | 0.89 | 0.51 | 0.96 | 0.80 | — | 0.70 |

Note: ECN values presented in Table 16.

TABLE 18. EFFECTIVE CARBON NUMBERS OF NMHC WITH $CH_4$ = 1.0 AS BASIS, APPLYING DAILY CALIBRATION

| | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 | RTI | NMHC Species Average | Rel. Spread Per Species |
|---|---|---|---|---|---|---|---|---|
| Methane ($CH_4$) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | ---- |
| Propane ($C_3H_8$) | (2) 0.63 | 0.52 | 0.56 | 0.49 | 0.48 | (1) --- | 0.54 | 0.28 |
| Ethylene ($C_2H_4$) | 0.58 | 0.47 | 0.47 | 0.38 | 0.42 | 0.52 | 0.47 | 0.43 |
| Propylene ($C_3H_6$) | 0.77 | 0.47 | 0.58 | 0.43 | 0.36 | 0.46 | 0.51 | 0.80 |
| Acetylene ($C_2H_2$) | 0.65 | 0.66 | 0.67 | 0.66 | 0.49 | 0.49 | 0.60 | 0.30 |
| Toluene ($C_7H_8$) | 0.86 | 0.48 | 0.55 | 0.44 | (3) 0.33 | 0.47 | 0.52 | 1.02 |
| Acetaldehyde(5) ($CH_3CHO$) | 0.74 | 0.28 | 0.25 | 0.24 | (4) 0 | 0.44 | 0.39 | 1.28 |
| Mean of NMHC(6) Per Instrument | 0.70 | 0.52 | 0.57 | 0.48 | 0.42 | 0.48 | 0.53 | 0.53 |
| $\frac{(ECN_{max}-ECN_{min})}{(ECN_{avg})}$ Per Instrument | 0.40 | 0.37 | 0.35 | 0.58 | 0.38 | 0.13 | | |

Notes:

(1) Instruments not on line when propane response determined.

(2) Cutter oven not operating properly; based on propane-with-no-methane samples.

(3) Calculated using toluene samples only; toluene/methane mix gave ECN = 0.1.

(4) Gave small negative or zero readings.

(5) Analysis showed decomposition to 60% acetaldehyde and 40% acetic acid.

(6) Excludes $CH_3CHO$. This mean value for ECN is based only on the species tested. It may not be the same for typical ambient air samples because of the difference in relative abundance of unsaturated hydrocarbons.

## TABLE 19. RESULTS OF CORRECTING NMHC TO PROPANE (8), USING DAILY CALIBRATION

| | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 | (7) RTI | NMHC Species Average | Relative Spread Per Species |
|---|---|---|---|---|---|---|---|---|
| Methane ($CH_4$) | 1.59 | 1.92 | 1.79 | 2.04 | 2.08 | 2.13 | 1.93 | 0.28 |
| Propane ($C_3H_8$) | (2) 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | (1) --- | 1.0 | ---- |
| Ethylene ($C_2H_4$) | 0.92 | 0.90 | 0.84 | 0.77 | 0.88 | 1.11 | 0.90 | 0.38 |
| Propylene ($C_3H_6$) | 1.22 | 0.90 | 1.04 | 0.88 | 0.75 | 0.98 | 0.96 | 0.49 |
| Acetylene ($C_2H_2$) | 1.03 | 1.27 | 1.20 | 1.35 | 1.02 | 1.04 | 1.14 | 0.29 |
| Toluene ($C_7H_8$) | 1.37 | 0.92 | 0.98 | 0.90 | (3) 0.69 | 1.0 | 0.98 | 0.69 |
| Acetaldehyde (5) ($CH_3CHO$) | 1.17 | 0.54 | 0.45 | 0.49 | (4) 0 | 0.94 | 0.60 | 1.20 |
| Mean NMHC ECN (6) | 1.11 | 1.00 | 1.01 | 0.98 | 0.87 | 1.03 | 1.0 | 0.24 |
| $\frac{(ECN_{max} - ECN_{min})}{ECN_{Avg}}$ Per Instrument | 0.41 | 0.37 | 0.36 | 0.59 | 0.38 | 0.13 | --- | ---- |

**Notes:**

(1) - (6) All notes from Table 18 apply.

(7) Use Toluene ECN = 1.

(8) Method of Correction

$$\frac{\text{ECN of NMHC from Table 18}}{\text{ECN of } C_3H_8 \text{ for that Instrument}}$$

= ECN (corrected).

## TABLE 20. EFFECT OF METHANE ON ECN OF NMHC, USING DAILY CALIBRATION

| | | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 | RTI |
|---|---|---|---|---|---|---|---|
| Propane: | with $CH_4$ | --- | 0.54 | 0.54 | 0.50 | 0.48 | --- |
| ($C_3H_8$) | no $CH_4$ | 0.63 | 0.50 | 0.57 | 0.47 | 0.47 | --- |
| Ethylene: | with $CH_4$ | 0.59 | 0.46 | 0.47 | 0.40 | 0.41 | 0.53 |
| ($C_2H_4$) | no $CH_4$ | 0.57 | 0.50 | 0.48 | 0.35 | 0.44 | 0.51 |
| Propylene: | with $CH_4$ | 0.77 | 0.47 | 0.56 | 0.44 | 0.37 | 0.44 |
| ($C_3H_6$) | no $CH_4$ | 0.76 | 0.46 | 0.62 | 0.40 | 0.36 | 0.57 |
| Acetylene: | with $CH_4$ | 0.69 | 0.65 | 0.69 | 0.69 | 0.46 | 0.49 |
| ($C_2H_2$) | no $CH_4$ | 0.61 | 0.67 | 0.65 | 0.63 | 0.51 | 0.48 |
| Toluene: | with $CH_4$ | 0.82 | 0.49 | 0.55 | 0.46 | --- | 0.47 |
| ($C_7H_8$) | no $CH_4$ | 0.84 | 0.48 | 0.55 | 0.41 | 0.33 | 0.47 |
| Acetaldehyde: | with $CH_4$ | 0.75 | 0.33 | 0.22 | 0.30 | 0 | 0.51 |
| ($CH_3CHO$) | no $CH_4$ | 0.72 | 0.24 | 0.26 | 0.18 | 0 | 0.37 |

Note: See notes on Table 18.

TABLE 21. RATIO OF $\frac{\text{ECN (no CH}_4\text{)}}{\text{ECN (with CH}_4\text{)}}$, USING DAILY CALIBRATION

| | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 | RTI |
|---|---|---|---|---|---|---|
| Propane ($C_3H_8$) | --- | 0.93 | 1.06 | 0.94 | 0.98 | --- |
| Ethylene ($C_2H_9$) | 0.97 | 1.09 | 1.02 | 0.87 | 1.07 | 0.96 |
| Propylene ($C_3H_6$) | 0.99 | 0.98 | 1.11 | 0.91 | 0.97 | 1.30 |
| Acetylene ($C_2H_2$) | 0.88 | 1.03 | 0.94 | 0.91 | 1.11 | 0.98 |
| Toluene ($C_7H_8$) | 1.02 | 0.98 | 1.00 | 0.89 | --- | 1.0 |
| Acetaldehyde ($CH_3CHO$) | 0.96 | 0.73 | 1.18 | 0.60 | --- | 0.73 |

Note: ECN values given in Table 20.

from 0.42 for the Bendix 8201 to 0.70 for the MSA 11-2 with a mean value of 0.53. As a measure of the variance in NMHC response a relative spread defined as the maximum ECN value minus the minimum ECN value divided by the average ECN value is used. A relative spread of 0.53 (53% of average) was seen in the mean value of the NMHC response for these instruments. By computing the average of the instrumental mean NMHC responses, an overall NMHC mean response of 0.53 was calculated. Comparing this to the 0.44 value from Table 14, daily calibration resulted in a 20% increase in the ECN values.

Considering the instruments individually, the MSA 11-2 had a uniformly high NMHC response with a mean NMHC value of 0.70 and relative spread of 40%. As was noted previously about 7.5 minutes was required for the toluene in this instrument. Response time was negligible for other species. The two Beckman Instruments, the Model 400 and 6800, gave ECN means of 0.52 and 0.57, respectively, and slightly more narrow spreads than the MSA; compound-to-compound response of the two instruments matched well. Lower ECN values were exhibited by the remaining three instruments, the Bendix 8200 and 8201 and the RTI prototype, which responded approximately the same with mean ECN's of 0.48, 0.42, and 0.48, respectively. The spread in the NMHC response of the RTI model was the lowest of any of the instruments. It was quite interesting to note the similarity between the two Beckman and two Bendix models since each of the two pair had identical FID's. The slightly higher response of the Beckman instruments may be the result of the slight differences of detector design or to operating conditions which the manufacturers suggest using - different flame conditions producing different HC responses. Time did not permit detailed study on the instruments to determine the exact cause.

Looking at the relative spreads on a per specie basis, toluene and acetaldehyde showed spreads greater than 100%. The problem with acetaldehyde has been discussed. The large spread with toluene resulted from the unusually low response of the Bendix 8201 and unusually high (compared to other instruments) response of the MSA 11-2. Propylene cause a similar response pattern although not quite as severe as toluene.

Methane is known to yield a higher response in FID's on a per-atom-carbon basis than most NMHC's. An effort to correct for NMHC response differences was made on the ECN data of Table 18. By noting that the mean value of the NMHC for all the instruments was 0.53 and the NMHC species averages for all the compounds (except $CH_3CHO$) were close to this value, particularly propane

(0.54), propylene (0.51), and toluene (0.52), the possibility of correcting the NMHC values presented itself. The ECN values from Table 18 were divided by the ECN of propane (since it is available as an NBS certified SRM grade) per instrument. The "corrected" ECN's are displayed in Table 19. The mean NMHC ECN's have converged toward 1.0, as they should have, and the relative spread of the mean NMHC ECN's is now 22% compared to the 53% for uncorrected ECN's. The average of the NMHC means was exactly 1.0. Note that the relative spreads per instrument and per specie have also converged somewhat.

The utility of using propane corrected response can be illustrated. The "uncorrected" NMHC is given in ppm, with the response to $CH_4 = 1.0$ as basis, by

$$\text{THC} - CH_4 = \sum_n (\text{ECN}_n) \cdot C_n \tag{11}$$

where $\text{ECN}_n$ is the effective carbon number of the nth specie and $C_n$ is actual concentration of nth specie. For "correcting" with the response to propane, the ECN for propane, determined during calibration by using a propane injection, as well as methane, would be used to divide into the difference obtained in (11). The maximum error would occur if the NMHC mixture consisted of a single component, the kth, whose ECN showed greatest deviation from propane. Therefore,

$$\sum_n Cn \times (\text{ECN}_n) = 0 \quad (n \neq k) \tag{12}$$

and

$$\frac{C_k \text{ECN}_k}{\text{ECN propane}} = \text{"corrected" NMHC} \tag{12}$$

which would give

$$\%\ \text{Error}_{\text{max}} = \frac{\text{ECN}_k - \text{ECN propane}}{\text{ECN propane}} \times 100\ . \tag{13}$$

The advantage of this correction is that $CH_4$ calculation can continue as is currently prescribed by the Federal Register. The only additional information required is the ECN value for propane for each particular instrument, and reliable propane standards are available, Furthermore, other NMHC ECN's than that of propane might be used if local situations warranted.

The possibility of methane affecting the NMHC response was examined. In Table 20, the ECN's are compared with and without a methane background. The ratio of ECN (no $CH_4$):ECN (with $CH_4$) is shown in Table 21, and no definitive trends were perceived as most of the ECN averages were within ±10% of each other.

Ambient Air Measurements

At the conclusion of the test phases on calibration stability and non-methane hydrocarbon response the analyzers were operated at about 72 hours, from 1600 hours August 28, 1976 through 1600 hours August 31, 1976, sampling ambient air at the Research Triangle Institute in Research Triangle Park, N. C. Hourly average data for methane and total hydrocarbons for the five commercial instruments are tabulated and presented in Appendix B.

The sampling arrangement for the ambient air analysis was as shown schematically in Figure 26. Air was inducted through an inverted funnel located about 2.4 meters (8 feet) above ground level. Suction was from a Metal Bellows Co. Model HB-151 pump through Teflon® tubing. Pressurized air from the pump, at a flow of about 20 liters per minute, was conducted by 0.64 cm (0.25 inch) diameter PTFE tubing for a distance of about 9.1 m (30 feet) prior to entry into the building where the instruments were housed. From the entry point to the laboratory housing the instruments, the tubing run was about 30.5 m (100 feet). The sampling bulb manifold was relieved to atmosphere in the laboratory through three unused ports, which maintained the manifold pressure near one atmosphere. Tubing runs of 3.0 m (10 feet) connected each instrument under evaluation to the manifold.

The RTI prototype was not used in this comparative evaluation because it could not be used in any "automatic" unattended mode.

All instruments spans were set just prior to this phase of the test, using 8.0 ppm $CH_4$ in air. In spite of this there is a discrepancy in readings - even on methane - in the first hourly average. Data on $CH_4$ response has been plotted in Figure 27. The curve at the top of this figure is the average instrument reading (ensemble hourly average), obtained from the responses of MSA 11-2, Beckman 6800, Bendix 8200 and Bendix 8201. The lower group of curves represent the ratio of individual

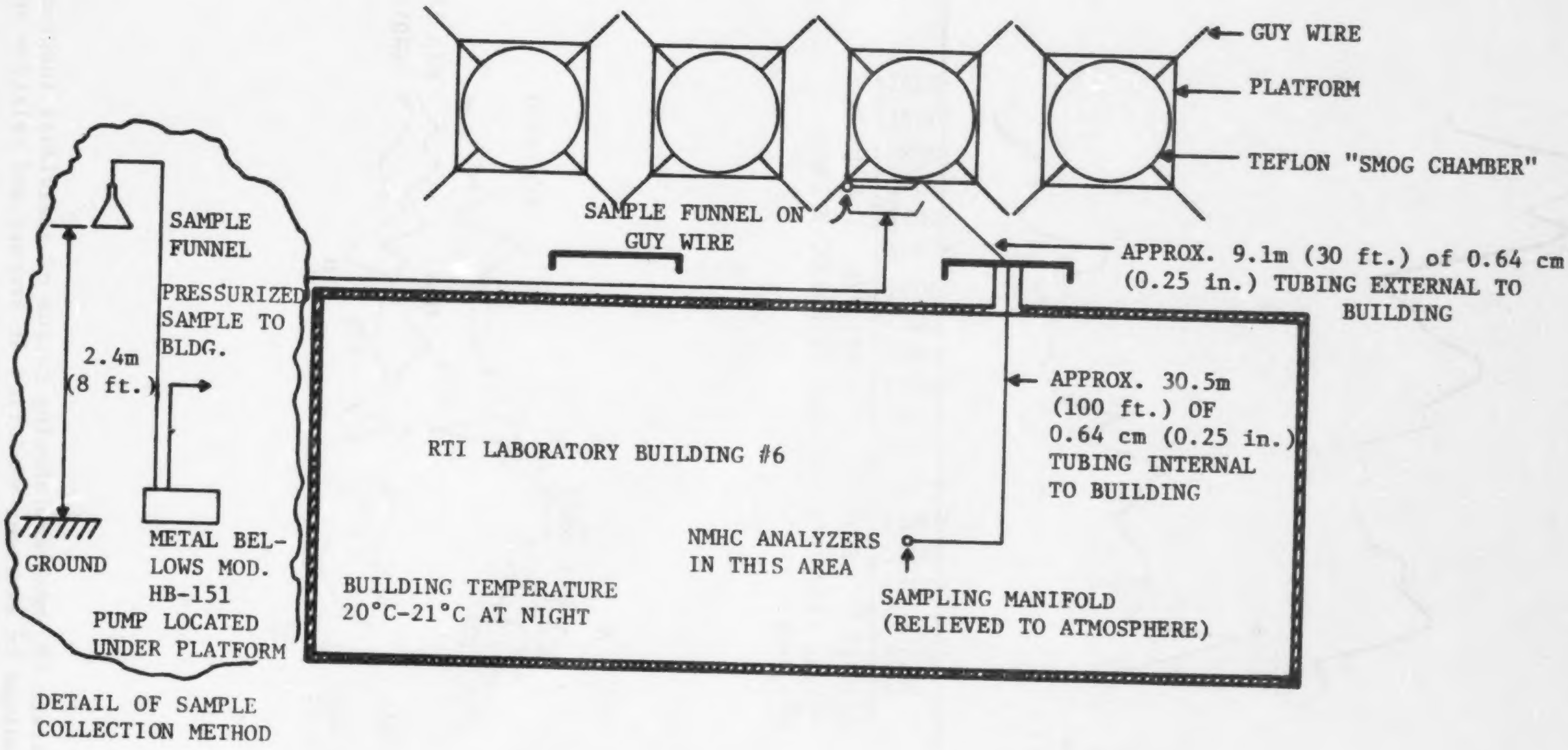
GUY WIRE
PLATFORM
TEFLON "SMOG CHAMBER"
SAMPLE FUNNEL ON GUY WIRE
APPROX. 9.1m (30 ft.) of 0.64 cm (0.25 in.) TUBING EXTERNAL TO BUILDING
APPROX. 30.5m (100 ft.) OF 0.64 cm (0.25 in.) TUBING INTERNAL TO BUILDING
RTI LABORATORY BUILDING #6
NMHC ANALYZERS IN THIS AREA
SAMPLING MANIFOLD (RELIEVED TO ATMOSPHERE)
BUILDING TEMPERATURE 20°C-21°C AT NIGHT
SAMPLE FUNNEL
PRESSURIZED SAMPLE TO BLDG.
2.4m (8 ft.)
GROUND
METAL BELLOWS MOD. HB-151 PUMP LOCATED UNDER PLATFORM
DETAIL OF SAMPLE COLLECTION METHOD

Figure 26. Sampling arrangements for comparative evaluation using ambient air.

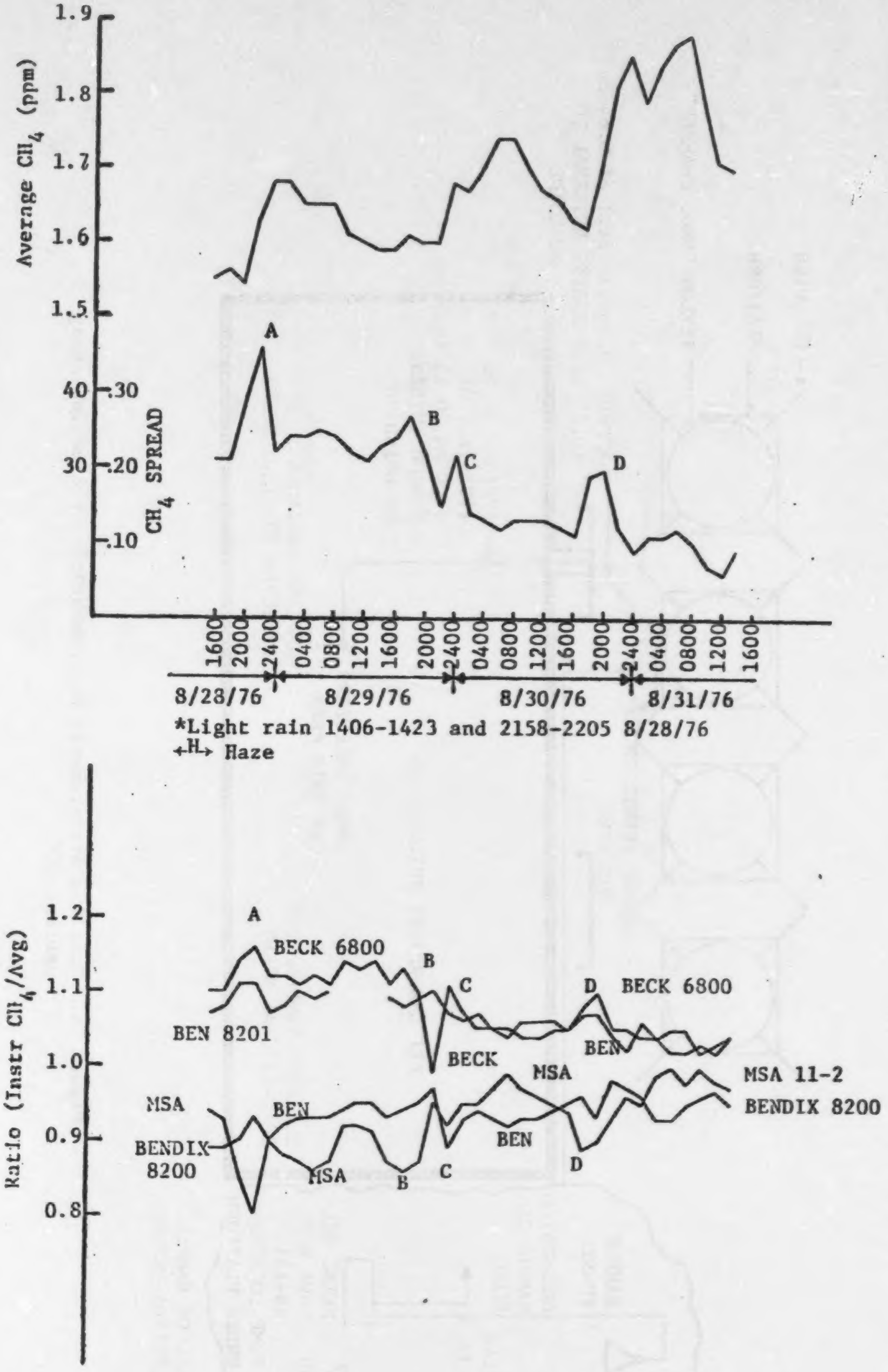

Figure 27. Average CH$_4$ response showing ratios of individual instrument readings to average, variation of average and relative spread.

instrument hourly average responses to the ensemble average plotted versus time. (The ensemble average ratio is taken as 1.0.)

Several interesting features occur in this data presentation. The first is the immediate discrepancy in $CH_4$ readings when these analyzers were exposed to ambient air. The spread is initially about ±10%, increasing to ±15%, -20% at about 6 hours after the start of the test, remaining in the order of ±15% for about 24 hours and then gradually decreasing to within about ±5% after about 65 hours exposure. The second feature is that two of the analyzers, Beckman 6800 and Bendix 8201, consistently gave higher than average readings while the other two analyzers, MSA 11-2 and Bendix 8200 consistently gave lower than average readings. A third feature is that the spread in readings did not appear to be strongly dependent on the ensemble average $CH_4$ reading. The curve in the middle of Figure 27 shows the relative spread, maximum reading minus minimum reading divided by the ensemble average.

Data on total hydrocarbon response is plotted in Figure 28. The middle curve shows the ensemble average THC reading. This was obtained by using hourly averages from all five analyzers, or however many were "on line" at a particular hour. The lower group of curves represent the ratio of instrument hourly average THC readings to the ensemble average THC value plotted versus time. The ensemble average ratio is taken as 1.0. Also shown is the relative spread in THC readings.

As was the case with the $CH_4$ response on at least two of the analyzers, the Beckman 6800 and the Bendix 8201, there appears to be a larger deviation from average during the first 8 to 12 hours after exposure to ambient air then later when such exposure has become "routine". The Beckman 6800 THC response, initially some 23% below average gradually rose to about 5 to 6% below average whereas the Bendix 8201 remained consistently at about 15% below average. Both the Bendix 8200 and Beckman 400 averages also fluctuated with respect to the ensemble average, but were usually closer. The Bendix 8200 average started at about 8% below ensemble average and rose to within ±5% for about 24 hours before drifting down to fluctuations around the -10% level for the remainder of the test period. The Beckman 400 average initially

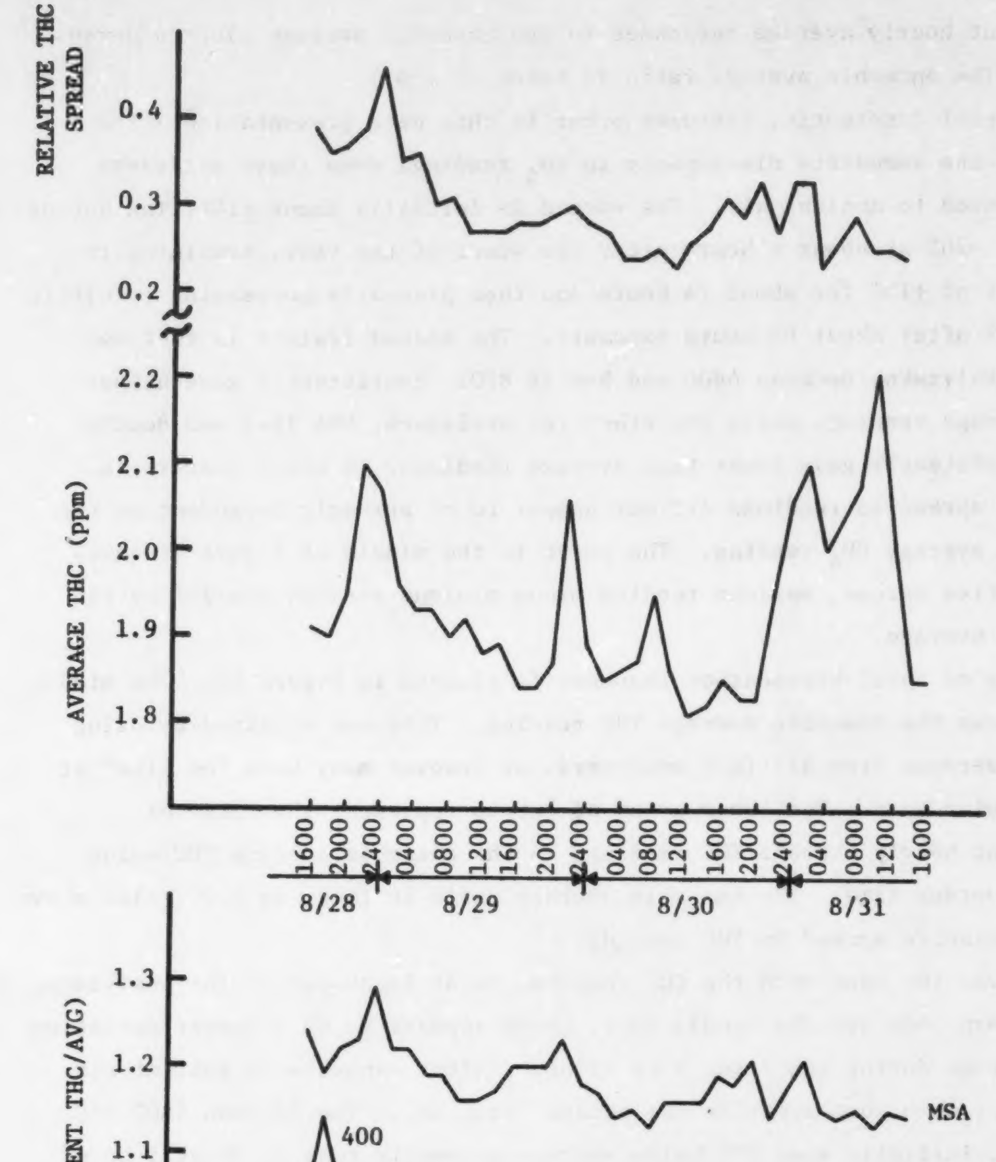

Figure 28. Average THC response showing ratios of individual instrument readings to average, variation of average and relative spread.

climbed to about 15% higher than the ensemble THC average. Then it dropped to about 10% below ensemble average before returning closer (5-10%) of the ensemble average over the last 40 hours of the test period. The MSA response was consistently higher than the ensemble average.

The consequence of Beckman 6800 and Bendix 8201 consistently having higher than average $CH_4$ readings and lower than average THC readings was either negative or very small positive NMHC values. This left only two instruments for which NMHC readings could be compared, the MSA 11-2 and Bendix 8200. Figure 29 gives a plot of three NMHC related (?) values versus time. The first is a fictitious average reading, labeled Δ Avg., obtained by subtracting the ensemble average $CH_4$ from ensemble average THC readings. The second is the MSA 11-2 NMHC reading and the third is the Bendix 8200 NMHC reading. The latter is usually in fair agreement with the Δ Avg., whereas the MSA 11-2 reading was at least twice the Δ Avg. or Bendix 8200 NMHC value.

Several other forms were used to plot the data in order to see if features could be found which would give some indication as to the cause of discrepancies.

Because the Bendix 8200 had exhibited relatively stable performance during the laboratory phase and the NMHC readings derived from its ($THC-CH_4$) readings were in reasonable conformity with the (Average THC - Average $CH_4$) values (see Figure 29), the $CH_4$ data and THC data were replotted with respect to the Bendix 8200 as a reference. Plots for $CH_4$ are shown in Figure 30, and plots for THC are shown in Figure 31. The spread in $CH_4$ readings (lower plot of Figure 30) still exhibits a strong downward trend over the test period with a series of peaks, labeled A, B, C, D. The Beckman 6800 and Bendix 8201 readings converged toward those of the Bendix 8200, while the MSA 11-2 $CH_4$ reading fluctuated back and forth with respect to the 8200 readings.

The spread in THC readings with respect to the Bendix 8200 readings shown in the lower curve of Figure 31, shows a trend of decline from 35% to 45% at the start of the test to about 25% to 35% at the end of the test.

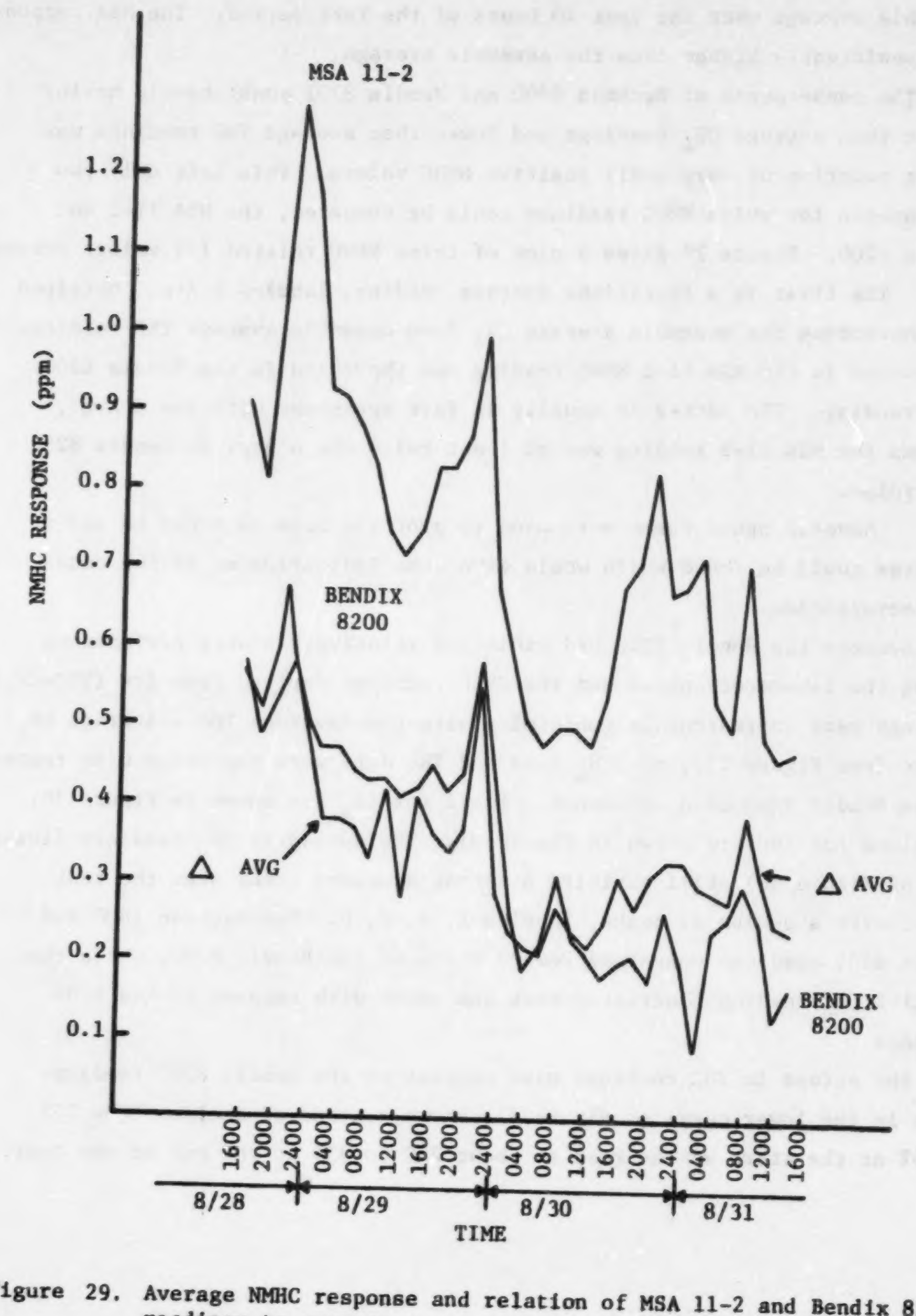

Figure 29. Average NMHC response and relation of MSA 11-2 and Bendix 8200 readings to average.

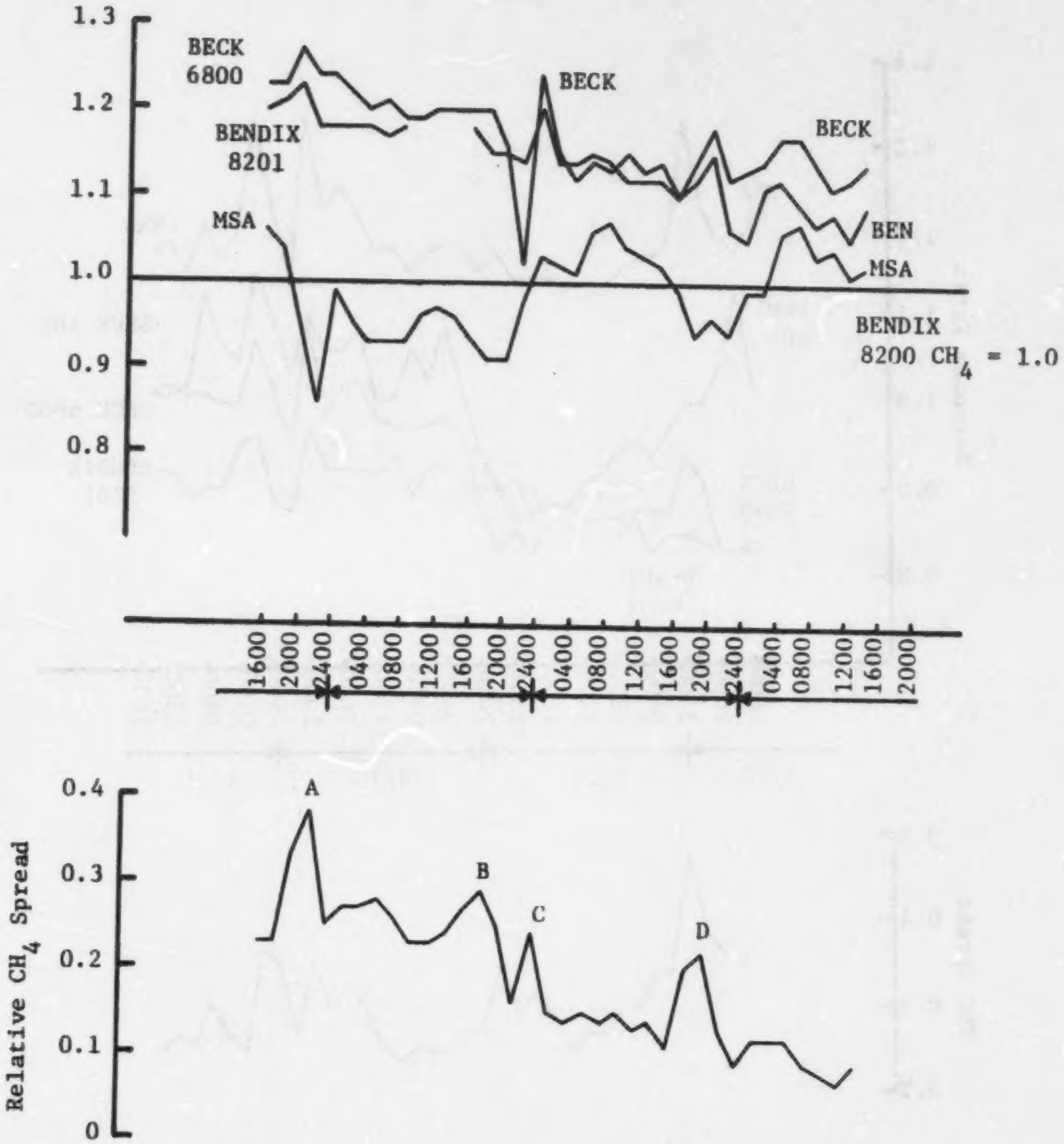

Figure 30. Ratios of individual instrument CH$_4$ readings to Bendix 8200 reading and relative spread of readings.

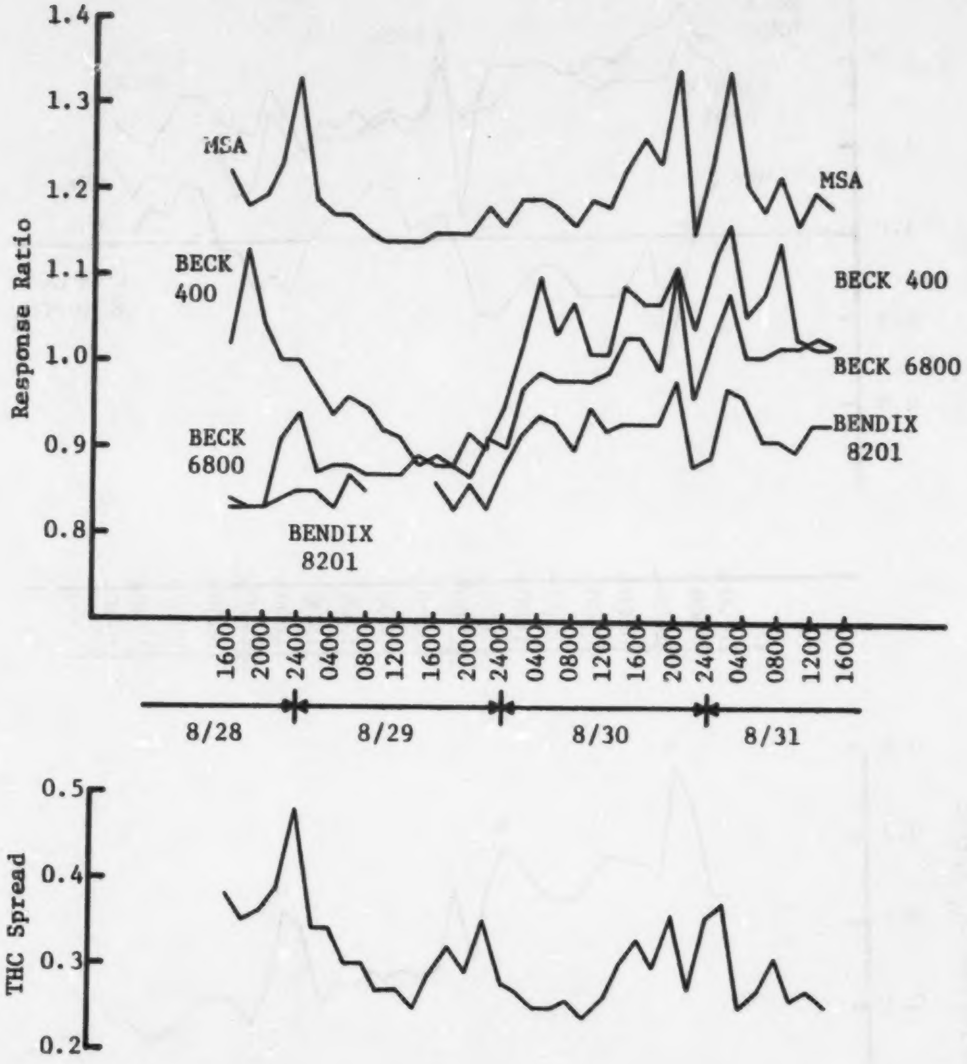

Figure 31. Ratios of individual instrument THC readings to Bendix 8200 reading and relative spread.

Inspection of the ratios of individual instrument THC readings to those of the Bendix 8200, the upper group of plots in Figure 31, shows similar trends to those noted previously in conjunction with Figure 28 with one exception. This is the MSA 11-2, whose trend with respect to the Bendix 8200 is relatively flat.

There did not appear to be any significant advantage in taking the Bendix 8200 $CH_4$ and THC readings as the "standard" for comparison.

Comparison of Laboratory and Ambient Air Tests

The higher THC readings of the MSA 11-2 are somewhat consistent with the data of Table 18 which showed that the MSA 11-2 gave higher response than the other analyzers to the NMHC species used in the laboratory evaluation. The consistently low ambient air THC readings of the Bendix 8201 are in agreement with the low average ECN obtained for this instrument in the laboratory tests. After the initial "acclimatization" period the Beckman 6800 THC readings rose within 18% to 20% of the MSA 11-2 readings (cf. Figure 31). This is consistent with the 23% higher average ECN response of the MSA 11-2 with respect to the Beckman 6800.

In the laboratory tests the MSA 11-2 average ECN values were about 50% larger than those for the Bendix 8200, whereas the ambient air values of NMHC for the MSA 11-2 were about twice that of the Bendix 8200. This was explainable in part by the lower $CH_4$ values of the MSA 11-2 which were obtained over the first 32-36 hours of the ambient air tests. However during the later portion of the ambient air evaluation, the $CH_4$ values of the MSA 11-2 increased to close to or slightly greater than those of the Bendix 8200 (of Figure 27).

The most obvious discrepancy between laboratory and ambient air readings occurred immediately after the instruments were placed on line sampling ambient air. This was the immediate spread in $CH_4$ readings of about 21% relative to the average although the instruments had just been made to agree using $CH_4$ to set their spans. This anomaly was pointed out in the discussion of Figure 27. It appears to be related to atmospheric moisture.

Data on meteorological conditions during the ambient air sampling test phase are given in Table 22. They are from official records of the

TABLE 22. DATA ON METEOROLOGICAL CONDITIONS
August 28, 1976 - August 31, 1976 from U. S. Weather Station, Raleigh-Durham Airport, North Carolina

| Date | Time | T (°C) | % Rel Humid | °C Dew Point | Station mmHg Pressure | Sky Cover % |
|---|---|---|---|---|---|---|
| 8/28 | 1553 | 29.4 | 55 | 19.4 | 752.3 | 100 |
| | 1753 | 27.8 | 67 | 21.1 | 752.1 | 100 |
| | 1952 | 26.1 | 70 | 21.1 | 752.1 | 100 |
| | 2153 | 24.4 | 79 | 20.5 | 752.3 | 100 |
| | 2353 | 23.9 | 79 | 20.0 | 752.7 | 100 |
| | Precip. 0.01 in equiv. RW 1406 - 1423 & 2158 - 2205 | | | | | |
| 8/29 | 0153 | 23.3 | 85 | 20.5 | 752.6 | 100 |
| | 0353 | 22.2 | 88 | 20.0 | 752.1 | 50 |
| | 0553 | 21.7 | 91 | 20.0 | 752.3 | 20 |
| | 0753 | 24.4 | 79 | 20.5 | 753.0 | 20 |
| | 0954 | 28.3 | 70 | 22.2 | 753.1 | 0 |
| | 1153 | 31.7 | 54 | 21.1 | 752.1 | 50 |
| | 1353 | 32.2 | 47 | 19.4 | 751.1 | 50 |
| | 1553 | 32.2 | 47 | 19.4 | 750.1 | 40 |
| | 1752 | 31.1 | 48 | 18.9 | 750.3 | 30 |
| | 1955 | 26.1 | 69 | 20.0 | 751.0 | 80 |
| | 2154 | 24.4 | 82 | 20.0 | 751.7 | 80 |
| | 2353 | 24.4 | 48 | 12.8 | 752.6 | 30 |
| | Zero Precip. Haze 0245-0745 | | | | | |
| 8/30 | 0154 | 22.8 | 44 | 10.0 | 752.9 | 40 |
| | 0353 | 21.1 | 53 | 11.1 | 753.1 | 50 |
| | 0553 | 20.0 | 57 | 11.1 | 754.1 | 90 |
| | 0752 | 20.5 | 55 | 11.1 | 755.0 | 100 |
| | 0956 | 22.2 | 46 | 10.0 | 756.3 | 60 |
| | 1155 | 23.3 | 37 | 7.8 | 755.8 | 20 |
| | 1352 | 25.0 | 27 | 4.4 | 755.3 | 0 |
| | 1553 | 25.5 | 23 | 3.9 | 754.8 | 40 |
| | 1752 | 23.9 | 24 | 2.2 | 754.4 | 90 |

## TABLE 22 (Continued)

| Date | Time | T (°C) | % Rel Humid | °C Dew Point | Station mmHg Pressure | Sky Cover % |
|---|---|---|---|---|---|---|
| 8/30 | 1953 | 18.3 | 38 | 3.9 | 755.0 | 50 |
| | 2154 | 13.3 | 66 | | 755.1 | 30 |
| | 2353 | 14.4 | 51 | 4.4 | 755.0 | 0 |
| | Zero Precip. No Haze. | | | | | |
| 8/31 | 0153 | 13.9 | 53 | 4.4 | 755.4 | 0 |
| | 0353 | 12.2 | 66 | 6.1 | 755.5 | 0 |
| | 0553 | 9.4 | 77 | 5.6 | 756.3 | 0 |
| | 0753 | 17.2 | 58 | 8.9 | 756.8 | 20 |
| | 0953 | 23.3 | 36 | 7.2 | 756.9 | 50 |
| | 1153 | 26.1 | 30 | 7.2 | 756.3 | 100 |
| | 1353 | 26.6 | 31 | 8.3 | 755.4 | 100 |
| | 1554 | 27.2 | 29 | 7.8 | 754.9 | 40 |
| | 1753 | 25.6 | 32 | 7.8 | 754.5 | 30 |
| | 1956 | 18.3 | | 10.0 | | |
| | 2153 | 17.8 | | 9.4 | | |
| | 2352 | 15.0 | | 9.4 | | |
| | Zero Precip. No Haze. | | | | | |

U. S. Weather Service Station at Raleigh-Durham Airport (RDU), which is located some six to seven miles from the instrument test site on the Research Triangle Institute campus. For several days preceding the ambient air sampling phase, the weather was typically hot with high humidity and low circulation, characteristic of late summer conditions in this area. Because of the low circulation it appeared to be opportune to obtain higher than normal hydrocarbon readings. However, the day after the ambient air sampling started, circulation increased, bringing unseasonably cool, dry air into the area. This circumstance fortuitously provided a change in test conditions which appears to be significant.

Air temperature (I) and dew point (II) data for the period 1600 August 28 to 1600 August 31, 1976 are plotted versus time in Figure 32. Also indicated on the plot are the occurrence (at the RDU Weather Station) of two brief rain showers, one about two hours prior to the start of the test and one that occurred at about 2200 on August 28. In addition the weather records noted hazy conditions during the morning hours 0245-0745 on August 29, 1976. Otherwise there was no other precipitation noted.

Plotted in Figure 32 along with the weather data is the spread in analyzer $CH_4$ (III) readings taken from Figure 27. The relationship between the spread in readings and the dew point is obvious. As the dew point decreases the spread in readings decreases. There is additional modulation which gives peaks A, B, C, and D in the "$CH_4$ spread" curve. Each of these peaks appears when the air temperature is decreasing, a period typically accompanied by the condensation of atmospheric water vapor. The decreasing air temperature at A' on the upper curve, during the night of August 28 was accompanied by a brief rainshower (at least at the RDU Weather Station) and appears to be directly related to peak A on the "$CH_4$ spread" curve.

The rising air temperature during the period 0600 to 1200 on August 29 is reflected inversely in the "$CH_4$ spread" curve. As the weather pattern began to change in the late afternoon and early evening of August 29, the dew point dropped considerably, aborting the build-up of peak B. However after passage of the frontal system, the decline in air temperature over portions B' and C' of the upper curve (Figure 32) apparently fostered sufficient condensation to result in peak C of the "$CH_4$ spread" curve.

As the air temperature rapidly decreased 10.6°C (19°F) over four hours (portion D' of the upper curve, Figure 32) during the late afternoon and

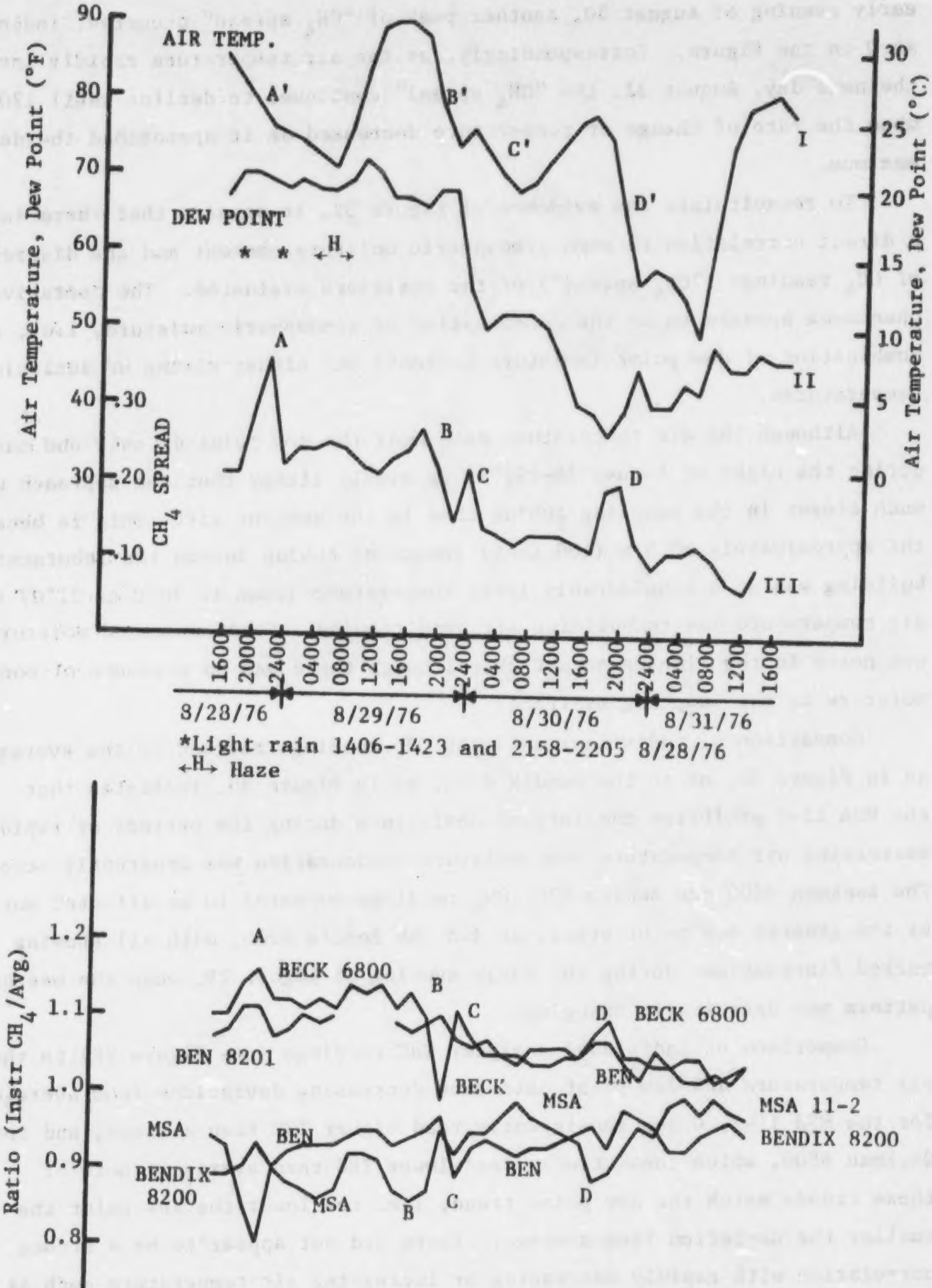

Figure 32. Plot of meteorological data showing relationship to relative spread of CH$_4$ reading.

early evening of August 30, another peak of "$CH_4$ spread" occurred, indicated as D on the Figure. Correspondingly, as the air temperature rapidly increased the next day, August 31, the "$CH_4$ spread" continued to decline until 1200 when the rate of change of temperature decreased as it approached the daily maximum.

To recapitulate the evidence of Figure 32, it appears that there is a direct correlation between atmospheric moisture content and the discrepancy of $CH_4$ readings ("$CH_4$ spread") of the analyzers evaluated. The operative phenomena appears to be the condensation of atmospheric moisture, i.e., a combination of dew point (moisture content) and either rising or declining temperatures.

Although the air temperature came near the dew point in only one case, during the night of August 28-29, it is highly likely that the approach was much closer in the sampling tubing than in the ambient air. This is because the approximately 30.5 m (100 feet) length of tubing inside the laboratory building was at a considerably lower temperature (down to 20°C to 21°C) than air temperature due to building air conditioning. Some condensed moisture was noted in the line on August 29, although there was no evidence of condensed moisture in the sampling manifold.

Comparison of individual analyzer $CH_4$ readings ratioed to the average, as in Figure 32, or to the Bendix 8200, as in Figure 30, indicates that the MSA 11-2 exhibited the largest deviations during the periods of rapidly decreasing air temperature when moisture condensation was apparently occurring. The Beckman 6800 and Bendix 8201 $CH_4$ readings appeared to be affected more by the general dew point trend, as did the Bendix 8200, with all showing marked fluctuations during the early evening of August 29, when the weather pattern was drastically changing.

Comparison of individual analyzer THC readings (see Figure 28) to the air temperature and dew point data show decreasing deviations from average for the MSA 11-2, which consistently read higher THC than average, and the Beckman 6800, which consistently read lower THC than average. Both of these trends match the dew point trend, i.e. the lower the dew point the smaller the deviation from average. There did not appear to be a strong correlation with rapidly decreasing or increasing air temperature such as that noted with the $CH_4$ readings.

A similar, but inverted, trend is detectable in the THC readings, Figure 28, where the ratio of the MSA 11-2 and Bendix 8200 THC to ensemble average THC tended to decrease with decreasing dew point whereas the Beckman 6800 THC ratio to ensemble average THC tended to increase with decreasing dew point. The Bendix 8201 THC did not appear to follow this trend. None of the analyzers tended to show the pronounced peaks that occurred with the $CH_4$ readings.

Granted this, it remains to be determined how condensable moisture affects analyzers in two different ways. As was pointed out in connection with Figure 27, two analyzers, the MSA 11-2 and Bendix 8200, consistently read lower $CH_4$ than average and two, the Beckman 6800 and Bendix 8201, consistently read higher $CH_4$ than average. In comparing these instruments there appear to be more similarity than differences in design for those which behave differently with respect to atmospheric moisture, and more difference than similarity in design for those which behave the same way with respect to atmospheric moisture. There appears to be only one seemingly insignificant item which the "low readers" shared and which the "high readers" lacked. This was an in-line particulate filter. The MSA 11-2 and Bendix 8200 have built-in filters. The other three instruments do not.

The condensation of water vapor on a surface provides a liquid film which is capable of taking a variety of gases into solution. The same can be said for a droplet of water in the air. The solubility of hydrocarbons in water is low, depending on relative polarity and molecular size, and it is well known that methane is soluble only to a limited extent in water. However, one hypothesis is that as atmospheric water vapor condenses it absorbs $CH_4$, among other gases. As an ambient air sample is drawn into an analyzer the steam will contain water vapor entrainment which tends to condense on the walls of the sample lines. If there is a particulate filter of high specific surface area in the gas stream, condensation can coat the filter fibers, providing a liquid film, depleting the gas stream. Alternatively, if there is no filter the condensation and absorption takes place on sample line walls. Thus an aliquot of sample in a, say 3 ml volume is enriched by additional gas as the sample is drawn into the heated sample loop. However, the opposite effect of atmospheric mositure on THC response, compared to $CH_4$ response, makes this hypothesis untenable.

Another hypothesis is that somehow the presence or absence of water vapor changes the flame dynamics. However, for four of the five instruments compared which could measure methane, the measurement includes stripping on an adsorbing column, which would be expected to remove the water vapor. In the MSA 11-2, of course, a catalytic oxidation step is used for NMHC stripping.

A third hypothesis is that the presence of condensation on the filter increases resistance to flow and decreases the sample flow rate (in the MSA 11-2) or sample pressure (in the Bendix 8200).

At this point it appears that none of these hypotheses are tenable and that further study must be undertaken to elucidate the mechanism relating response variations with atmospheric water.

## CONCLUSIONS

The comparative evaluation has yielded data which support the following conclusions:

1. Zero drift of these instruments is apparently not a significant problem.
2. Span drift in excess of the EPA performance guideline 24-hour specification of 5% can be a problem, and expectation of calibration stability longer than 24 hours is unrealistic.
3. Precision is within EPA specifications when span drift is taken into account.
4. There are significant differences in response to non-methane hydrocarbons, both on an intra-instrument and inter-instrument basis.
5. The NMHC response differences are ameliorated by using propane response as a basis for correcting effective carbon number.
6. The field analyzers are of complicated design and construction and are subject to a variety of maintenance problems. As expected, one of the components most susceptible to malfunction is the automatic switching valve.
7. Materials of construction of gas lines and values as well as filters and columns can have a significant affect on some of the heavier, or more reactive hydrocarbon species.

8. Instruments made to agree in the laboratory through calibration with dry $CH_4$/air mixtures, immediately start to display differences in response when exposed to the atmosphere.
9. Variations in instrument response to both $CH_4$ and THC are apparently related to atmospheric moisture content. The mechanisms which cause this relationship are not understood at present.

Using the information developed in this and prior sections of this report some conclusions can be drawn about the sources of error which militate against measurement accuracy with the present Federal Reference Method. These are presented in the next section.

## SECTION 8

## SOURCES OF ERROR WITH PRESENT METHOD

The information and data developed in previous sections of this report, combined with that obtained from prior studies (3, 4), provide the basis for discussion of the sources of error in the measurement process of the present Federal Reference Method for the determination of non-methane hydrocarbon concentration in ambient air. For convenience this analysis is divided into four categories which correspond to the interacting components of the measurement procedure: instruments, reagents, procedure and operators.

### INSTRUMENTS

Presently available commercial analyzers designed for measurement of non-methane hydrocarbons in ambient air via a subtractive technique (i.e., total hydrocarbon "reading" minus methane "reading") are subject to several problems which contribute to errors in ambient air NMHC measurement. These will be discussed in the categories: calibration stability, NMHC response, signal processing, and instrument specifications.

### Calibration Stability

Electronic zero (baseline) for the instruments evaluated in this study was relatively stable and within EPA performance guideline specifications. However, span drift of greater than ± 5% per 24 hours was experienced for significant fractions of operating time. Precision for repeated injections over relatively short periods of time (typically 3 to 4 hours) was generally very good, well within EPA specifications. This performance indicates that the automatic baseline correction feature of the commercial analyzers works well, but the FID ionization process and/or the electronic gain of the signal amplifiers is not as stable as desired.

In Section 6 when the response of manufacturers to the question about selection of $H_2$ and carrier air settings was summarized, it was apparent that few (if any) have carried out detailed studies of the effects of flow variations on the response of their FID designs. One notable exception is for the Beckman 400, the operating manual for which has data showing the effect of

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$H_2$ and carrier air flows (actually given in terms of supply pressures) on methane response. The common method of obtaining constant flow control is to use a pressure regulator in conjunction with a section of capillary tubing maintained at essentially constant temperature or to use a porous resistor. Instruction manuals give a range of pressure settings for a given gas stream flow; although in some cases specific pressure values are given for the individual instruments. Alternatively a range of flows may be given, to be measured with a flow meter (such as a "bubble" flow meter). Once these settings are made, presumably they are fixed until some event such as a major overhaul, de-activation, storage and re-activation, or some similar occurence requires a set-up "from scratch".

As shown in Section 4, the response of an FID to methane (and presumably other hydrocarbons) depends upon the $H_2$/carrier flow ratio. If $H_2$ and carrier air flows are not set in the vicinity of maximum response - which is a relatively broad peak for each, the response may vary significantly with variations in the flow of either gas stream. Therefore, it appears that when FID response is not peaked with respect to $H_2$ and carrier gas flows, stable control of these flows becomes an essential factor in maintaining stable instrument response.

For those cases where flow control is based on the attainment of critical flow conditions--i.e., the attainment of sonic velocity (32) in a capillary tube--the gas mass flow rate is given by (33)

$$Q_{max} = C_0 A_2 P_1 \left[\frac{gM\gamma}{RT}\left(\frac{2}{\gamma+1}\right)\frac{\gamma+1}{\gamma-1}\right]^{1/2} \times 10^{-3} \text{ kilograms per second} \quad (14)$$

where $C_0$ is a dimensionless discharge coefficient, $A_2$ is the cross sectional area of the capillary, $P_1$ the upstream pressure, g the acceleration due to gravity, M the gas molecular weight, R the gas constant, T the gas absolute temperature, and $\gamma$ the ratio of specific heat at constant pressure to specific heat at constant volume for the gas. For a given gas and capillary size, the flow rate is directly proportional to the upstream pressure, $P_1$, and inversely proportional to the square root of temperature. Therefore, to a good approximation, the fractional change in flow rate is directly proportional to the fractional change in upstream pressure and is directly proportional to one-half the fractional change in gas stream temperature. Therefore, if R represents

FID response to a given species--e.g., methane--since

$$\Delta R = \frac{\partial R}{\partial Q_{H_2}} \Delta Q_{H_2} + \frac{\partial R}{\partial Q_{Air}} \Delta Q_{Air} \qquad (15)$$

then

$$\Delta R = \left(\frac{\partial R}{\partial Q_{H_2}}\right) Q_{H_2} \left(\frac{\Delta P}{P} - \frac{1}{2}\frac{\Delta T}{T}\right)_{H_2} + \left(\frac{\partial R}{\partial Q_{Air}}\right) Q_{Air} \left(\frac{\Delta P}{P} - \frac{1}{2}\frac{\Delta T}{T}\right)_{Air} \qquad (16)$$

where the partial derivatives with respect to $H_2$ and carrier air flows represent the sensitivities of response to these factors, which, of course depends upon the operating point values of the variables.

When critical flow conditions do not occur, the flow depends upon pressure drop. This situation usually occurs when the sample is being inducted into sample loops or is being routed through the stripper column or through the tubing leading to the FID. In these cases the flow rate is given by

$$Q = \frac{GM}{T} \left(P_1 - P_2\right) \left[1 + \frac{P_1 - P_2}{2P_2}\right] \qquad (17)$$

where G is the conductance of the flow path (34). Condutance depends upon the flow geometry and the viscosity of the gas, which depends on the temperature. As with the case of the critical orifice, it is essential that both the gas temperature and the pressure be held constant if the flow is to be constant.

With present analyzer designs there is no provision for direct flow measurement with feedback control to maintain constant flow. The Beckman 6800 and Bendix 8200 both have rotameters for measurement of sample, carrier air and support air flow rates. Hydrogen flow is not monitored. While the accuracy of rotameters leaves a lot to be desired, they are useful as flow indicators and should be routinely checked to assure that flow rates are stable. The present Federal Reference Method, as well as equivalent procedures, specify an overall calibration stability without specifying the component drifts which influence this stability. There is no need to specify the latter if the overall stability is as specified. However, at present there does not appear to be any simple, short method to check stability.

In addition to electronic factors and flow control factors in response stability, there are other effects which influence flame kinetics. Atmospheric pressure variations were found to have a small effect on the $CH_4$ response of the RTI-designed FID, ranging about 2% for the normal range of atmospheric pressures (cf. Figure 12). This is probably representative for the instruments now available. A more serious problem is that of atmospheric water vapor. A change from 10°C to 30°C dew point gave about 5% increase in $CH_4$ response of the RTI GC-FID design (cf. Figure 23) and atmospheric moisture variations apparently significantly influenced commercial analyzer response, as was discussed in the previous section of this report. Any recommended measurement method should take such possible effects into account.

### Non-Methane Hydrocarbon Response

The laboratory evaluation reported in Section 7 demonstrated that there are significant differences in response of the commercial analyzers to non-methane hydrocarbons, even when propane response is taken as the basis for comparison rather than methane. If the NMHC species distribution remained relatively constant, a weighted average response factor could be used and agreement maintained. Since the species distribution does not remain constant, however, large discrepancies occur. One alternative approach would be to convert all of the NMHC to methane and measure the converted $CH_4$ to obtain directly NMHC as equivalent $CH_4$. In view of the experiences reported in Section 7, it would appear that if such alternative approaches are to be evaluated, they should be done so with realistic synthetic gas mixtures which include water vapor and $CO_2$.

Work has recently been reported (35, 36) in which the effect of sample flow rate and fuel composition on FID response to NMHC relative to that for $CH_4$ was studied. Reschke (35) undertook a study to improve instrument-to-instrument correlation for Beckman 400 hydrocarbon analyzer instruments, studying the effect on response to methane, ethane, propane, ethylene, propylene, benzene, toluene, and acetylene in air of burner flow parameters, fuel type and composition. Because this work was directed to automobile emissions study the hydrocarbon concentrations were very large, 150-200 ppm range, compared to those in ambient air. As a result of his investigation Reschke recommended that the sample flow rate be set to a minimum value (about 5 $cm^3$/minute), that a mixed composition fuel be used (40% $H_2$, 60% He), that the fuel flow rate to the burner be set high (100-120 $cm^3$/minute) and that the support air flow rate be set high (four times the fuel flow rate). He points out the importance of setting the burner flow rates of each instrument to the same value to achieve good correlation.

Black and High (36) reported a similar study, comparing the effect on NMHC analysis uniformity of various fuel mixtures, using exhaust gases from 22 vehicles, and comparing their results to those obtained with a species-by-species analysis by a laboratory gas chromatograph. These authors also concluded that a 40% $H_2$, 60% He fuel mixture was the most universally applicable for the THC analyzers, Beckman 400 and Beckman 108, used in their work.

These studies indicates that the proper choice of fuel composition and burner flow conditions will greatly improve uniformity of NMHC response and instrument-to-instrument correlation for instruments of the same type. Whether or not a single fuel mixture composition can be found which will improve agreement between FIDs of different design is a matter that can only be determined by further research. However, it should be pointed out that the achievement of NMHC response uniformity at the higher concentration levels of automotive sources is obtained in a tradeoff with sensitivity. It is possible that the reduced sensitivity might not be practicable for ambient air monitoring. This also is a subject for further research.

The two references cited are just a small indication of the intensive work that has been done to determine and correct the source of NMHC measurement discrepancies in automotive emissions monitoring. The reader is referred to the large body of literature generated by the automotive emissions measurement specialists, reported chiefly through EPA, the Society of Automotive Engineers (SAE) and the Bureau of Mines.

Signal Processing

The present method of using strip chart data and graphical conversion to obtain NMHC is highly inaccurate and time consuming. Although strip chart recorders probably contribute the smallest errors in the measurement system (cf. Appendix C), the graphical method used to extract data from the charts and convert to concentration units is subject to error because of the imprecision of scale measurement and the tedium which can lead to errors in interpretation. The difficulties in quantitating the difference in two numbers of approximately the same magnitude are well known.

Because changes in column conditions can cause peak shape changes, the use of peak height rather than peak area as a measure of concentration is subject to error. The availability of high stability, accurate analog integrators makes the measurement of peak area routinely achievable. Furthermore, the availability of relatively inexpensive analog-to-digital (A/D) converters and digital arithmetic circuitry offers an economical as well as reliable method of converting analog signals from the FID to digital form for arithmetic manipulation. The resulting digital signals can be used to drive printing data loggers or be transmitted by line to a central data collection system or be stored on magnetic tape for later processing. If it is desired to use peak shape as a diagnostic tool to check on proper column operation, an auxiliary analog output can be provided with a signal obtained prior to the A/D converter for presentation on a strip chart or memory trace cathode ray oscilloscope. Digital printout has advantages of accuracy, speed and presentation of the data in the format in which it is normally reported.

Any recommended standard practice endorsed or promulgated by EPA should include these signal processing improvements.

### Instrument Specifications

As with most items instrument specifications are subject to caveat emptor. Instruments should be set up in strict accordance with the instruction manual and tested to assure conformity with specifications. Generally any serious problems will be apparent within a short time. An equally important practice is to periodically check to make sure that specifications are still being met.

## REAGENTS

Problems with gas mixtures used to calibrate air monitoring instruments are not confined to those for hydrocarbon analysis alone. A recent symposium (37) has dealt with various aspects of this problem. In regard to so-called zero air it was pointed out (38) that this could contain varying, and unspecified, amounts of water vapor and $CO_2$. Additionally the analysis provided by the gas supplier may be faulty. As an example, it has been reported (38) that in zero gas certified by suppliers as having 0.1 ppm max THC as methane, four out of six cylinders contained significantly more, with one having greater than 0.5 ppm THC content.

Analysis error can be significant for span gas mixtures as well. Such analyses are usually carried out on commercial THC instruments which are calibrated with NBS propane SRM's (since a methane SRM is no longer available from NBS). As has been demonstrated abundantly in this report, FID response depends upon the HC species and the operating conditions. In addition to this source of error, the use of contaminated gas lines and regulators can contribute a highly variable background. Scott and Marrin (38) have reported that uncleaned regulators can give (apparent) methane concentration from 0.07 to 1 ppm. One further problem is the stability of calibration gas mixtures, particularly in the low ppm range. This has recently been discussed by Wechter and Greico (39).

## Calibration Gases

The errors in "zero" air and span gas concentration determinations introduce bias error into the measurements performed on instruments calibrated with these gases. In order to assess this contribution to the overall error, it will be assumed that the errors discussed fall on a normal distribution curve when expressed as percent of full scale (40). The "calibration hierarchy" (in Dieck's terms (40)) involves three stages, which are shown in Figure 33. The total uncertainty is given by

$$\varepsilon_S = b + 2S \tag{18}$$

where b is the NBS measurement bias and 2S is the quadruture sum of the precision errors due to instrument variation that includes 92% of data. This uncertainty provides an estimate of the measurement error due to span gas inaccuracy.

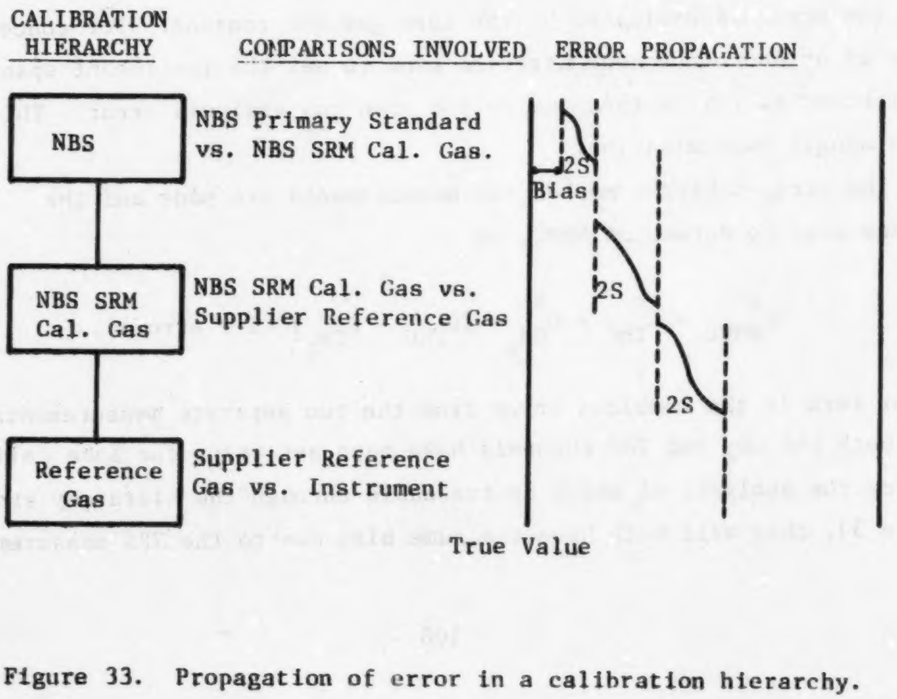
CALIBRATION HIERARCHY
COMPARISONS INVOLVED
ERROR PROPAGATION
NBS
NBS Primary Standard vs. NBS SRM Cal. Gas.
NBS SRM Cal. Gas
NBS SRM Cal. Gas vs. Supplier Reference Gas
Reference Gas
Supplier Reference Gas vs. Instrument
2S
Bias
2S
2S
True Value

Figure 33. Propagation of error in a calibration hierarchy.

The effect of THC content of zero air is to shift the calibration as shown in Figure 34. The relationship of the apparent concentration, $C_u^*$, of an unknown determined by using the span gas of "certified concentration" (i.e., apparent) $C_s^*$ and a zero air containing THC at a concentration $C_{10}$, is

$$C_u^* = \frac{C_u - C_{10}}{C_s - C_{10}} C_s^* \tag{19}$$

or

$$C_u(1 + \varepsilon_u) = \frac{(1 - C_{10}/C_u)}{(1 - C_{10}/C_s)} C_s (1 + \varepsilon_s) \tag{20}$$

where $\varepsilon_u$ is the error in the measurement of the true concentration of the unknown, $C_u$ and $\varepsilon_s$ is the error in the span determination, given by equation (18). It should be pointed out that this portrayal of calibration shift does not take into account any differences in response to different NMHC components in the zero and span gas. Such differences add to the error when readings from different instruments are compared. From equation (20) it can be seen that the error for a single measurement will depend on the residual THC in the zero air, the error in analysis of the gas concentration used to span the instrument, and the relative location of the measured concentration on the scale. For small concentrations of the unknown the error is dominated by the zero gas THC content. For concentrations at or above the concentration used to set the instrument span, the dominant error source is that due to the span gas analysis error. This is for a single determination.

In the strip-subtract method two measurements are made and the difference used to determine NMHC, or

$$C_{NMHC}^* = C_{THC}^* - C_{CH_4}^* = (C_{THC} - C_{CH_4}) (1 + \text{error}) . \tag{21}$$

The error term is the combined error from the two separate measurements. If the span of both the $CH_4$ and THC channels have been set using the same calibration gas source the analysis of which is traceable through the hierarchy shown in Figure 33, they will both have the same bias due to the NBS measurement

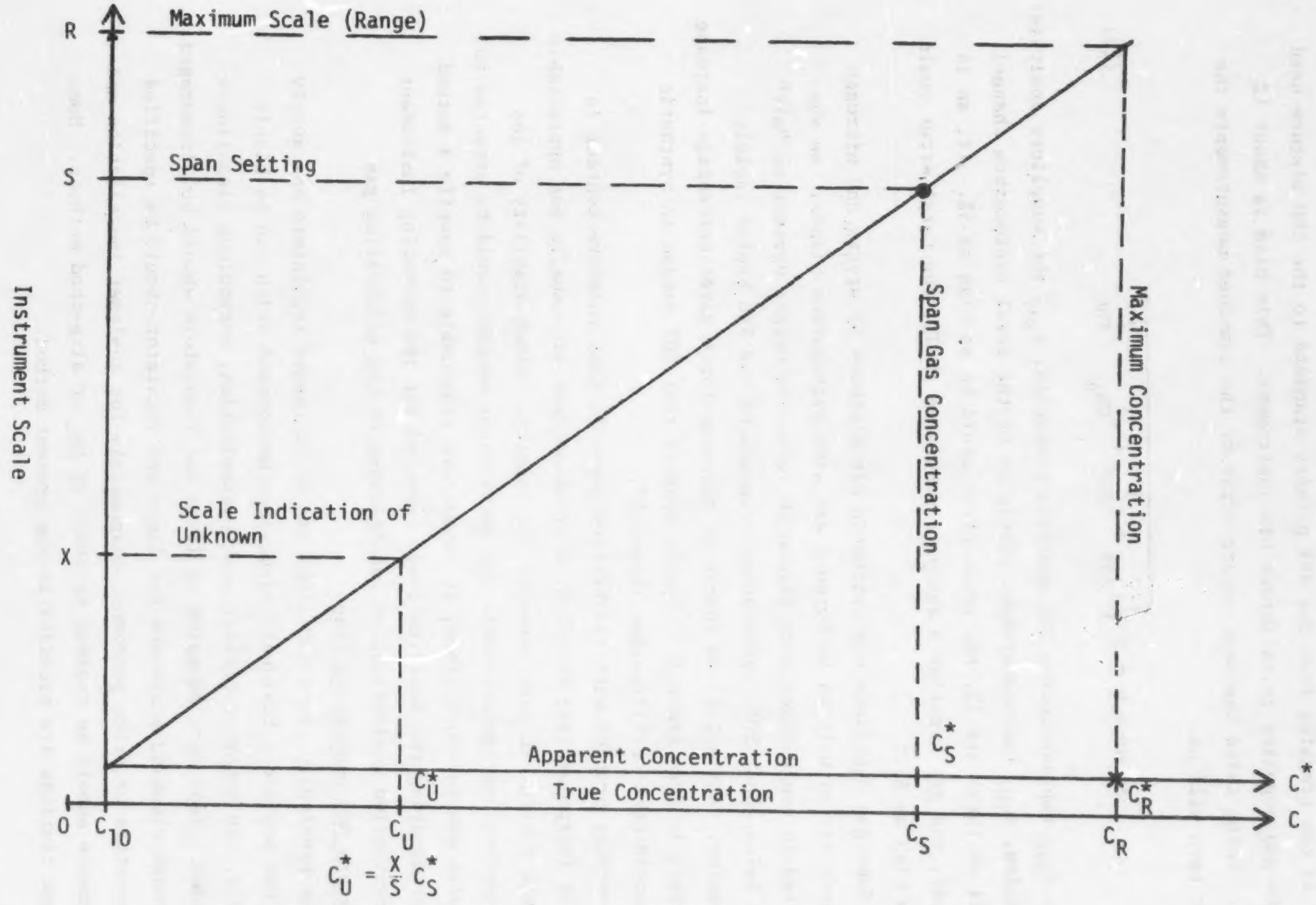
Maximum Scale (Range)
Span Setting
Scale Indication of Unknown
Instrument Scale
R
S
X
0
$C_{10}$
$C_U$
$C_U^*$
$C_S$
$C_S^*$
$C_R$
$C_R^*$
$C$
$C^*$
Apparent Concentration
True Concentration
Span Gas Concentration
Maximum Concentration
$C_U^* = \frac{X}{S} C_S^*$

Figure 34. Relation of instrument scale, calibrated on the basis of apparent concentrations for zero gas and span gas, to true hydrocarbon concentration.

bias in the transfer from the NBS primary standard to the SRM mixture used by the gas supplier to calibrate his instrument. This bias is about 1% (38). Using twice the mean square error of the combined measurements the error term will be

$$\text{error} = b + 2\sqrt{\varepsilon_{NBS}^2 + \varepsilon_{SUP}^2 + \varepsilon_{CH_4}^2 + \varepsilon_{THC}^2} \qquad (22)$$

where $\varepsilon_{NBS}$ represents the NBS analysis precision, $\varepsilon_{SUP}$ the suppliers analysis precision, $\varepsilon_{THC}$ the measurement precision of the total hydrocarbon channel. If all of these are 1%, the total error could be as high as 5%. If, as is typical, the gas supplier's analysis precision is 2%, the total error could be as high as 6.3%.

Some gas suppliers use synthetic air mixtures of oxygen and nitrogen for zero air as well as background air with hydrocarbon blends. As was reported in conjunction with Figure 20, when the oxygen content of "air" drops below about 20%, hydrocarbon response of the FID begins rapidly decreasing. Above 20% the change in response for a given percentage increase in oxygen is more gradual. Thus it appears that 20% oxygen in synthetic air should be a certification threshold.

Another problem with calibration gases is that moisture content is usually (purposefully) very low, whereas ambient air usually has appreciable moisture content in many areas of the country. Since stability of gas mixtures has been questionable and water vapor content could be expected to vary with ambient conditions, it seems more reasonable to specify a method of approximating the humidity range expected for the operating instrument by a controlled humidification conditioning of the calibrating gas.

## Regulators and Connecting Lines

As previously cited (38), the use of uncleaned regulators and supply lines can provide a residual hydrocarbon background which can be highly variable. In order to prevent such contamination, scrupulous cleanliness is needed. Impromptu swapping of lines and regulators should be discouraged. A thorough cleaning procedure for lines and regulator should be specified and operators or other personnel responsible for analyzer installation and maintenance should be trained to avoid *ad hoc* or slip-shod methods. None of these cautions are provided in the present method.

## Operating Reagents

The present Federal Reference Method specifies the purity of operating reagents--for example, support air, carrier air or other gases, hydrogen fuel--in terms of their total hydrocarbon content. As has been discussed at length above, gas supplier certifications should be at least spot checked to assure confidence. The effect of various levels of hydrocarbons in operating reagents was not checked during the present investigation, so no quantitative statements can be made about effects. However, good practice would be to check calibration (zero and span) each time an operating reagent supply is changed and to recalibrate if necessary.

## PROCEDURE

The present Federal Reference Method is limited to one instrumental approach only. A less restrictive specification that allows for alternative instrumental methods has been reported (22) but has not yet been promulgated for hydrocarbon analyzers. Several instruments which embody alternative methods are currently commercially available or nearing availability. These are:

1. MSA 11-2 which uses continuous reading dual FIDs,
2. Hewlett Packard which uses a backflush method to obtain NMHC directly,
3. Byron Instruments which converts all hydrocarbons to $CH_4$.

Of these only the MSA 11-2, which has been available for several years, was evaluated along with several strip/subtract type analyzers (the Federal Reference Method) in this study. With this exception, the performance of these alternative methods via-à-vis the strip/subtract method using ambient air has not been reported.

## Specification of Instrument Performance

The specifications for NMHC analyzers published in the performance guidelines (22) appear to be more realistic than those in the present Federal Reference Method. A comparison is given in Table 23. There are no specifications in the Federal Reference Method on noise, interference equivalents, zero drift, span drift or response times. These could be construed to be inherent in the accuracy requirement of 0.2 ppm (1% of full scale range of 20 ppm). The latter is unrealistic, however, in terms of calibration reagent concentration errors, span drift, and other error sources discussed previously.

TABLE 23. COMPARISON OF SPECIFICATIONS IN EPA PERFORMANCE GUIDELINES (22) WITH THOSE OF FEDERAL REFERENCE METHOD (1)

| Performance Parameter | Units | Performance Guideline Value | Federal Reference Method Value |
|---|---|---|---|
| Range | ppm | 0-5 | 0-20 |
| Noise | ppm | 0.05 | No specification |
| Lower Detectable Limit | ppm | 0.1 | 0.1 |
| Interference Eq. | | | |
| Each Interferent | ppm | ±0.1 | No specification |
| Total Interferent | ppm | ±0.2 | |
| Zero Drift, 12- and 24-Hour | ppm | ±0.2 | No specification |
| Span Drift, 24-Hour | percent | ±5 | No specification |
| Lag Time, Rise Time, Fall Time | minutes | 10 | No specification |
| Precision | ppm | 0.3 | 0.1 |
| Accuracy | ppm | No specification | 0.2 |

Specification of Reagents

One of the most apparent lapses in calibration gas specification is the failure to specify air as the gas containing $CH_4$ at the desired calibration levels. As noted in the Scott report (3) the use of methane in other than air for calibration yielded large measurement errors.

A second problem is the use of $CH_4$ to set the span of both the methane and total hydrocarbon channels with no consideration given for NMHC response differences. As shown in Section 7, there is much better agreement between analyzers when propane is used as the basis for comparison of NMHC response.

A third problem is the reliance upon gas supplier certification for the $CH_4$ and THC values. Deviations can lead to significant errors. Some method is needed for verification of supplier's analyses. One method is to cross-check using the "old" (nearly depleted) reagents and then the "new" to see if any obvious inconsistencies arise. Another method is to participate in periodic "round-robin" tests using specially prepared gases to check calibration. A third is to conduct analyses on all incoming gases with a reliable analytical grade gas chromatograph. The latter is the most rigorous, but also the most expensive, and for most monitoring sites probably out of the question.

### Calibration

The calibration procedure of the Federal Reference Method is based on the use of strip chart recorders for readout. It should be re-written to take into account the possible use of digital readout.

A noticeable lack is the failure to specify how often calibration should be checked and the permissible deviation beyond which re-calibration would be required.

### Maintenance

Except for suggesting stripper column replacement for every 2 months of operation, there are no maintenance cautions or requirements. As was pointed out in Section 7, malfunctions are a common occurrence, particularly with the moving parts of the automatic analyzers. Manufacturers generally supply maintenance and trouble-shooting procedures in their instruction manuals. This information can be used to formulate a routine preventive maintenance schedule. Such procedures, plus routine calibration checks, could be very advantageous in increasing the yield of credible data.

## OPERATORS

Even though NMHC analyzers are for the most part "automatic" and "continuous" (or continual), reliable data collection depends heavily upon the presence of trained, pragmatic operators and the exercise of supervision over monitoring operations.

### Training

Ambient air analyzers are sophisticated instruments which rely upon a variety of physical and chemical principles of operation. From the basic sensing principle through electronic and electromechanical components, a wide variety of technology is used to accomplish the measurement. If these instruments are to be properly used to gather reliable data, they must be placed into operation and be kept operating by personnel who understand their functionality and idiosyncrasies. Since few organizations are

## References

1. 40 CFR Part 50, Appendix E--Reference Method for Determination of Hydrocarbons Corrected for Methane. Federal Register 36 (84): 8198, April 30, 1971.
2. Decker, C. E. Research Triangle Institute. Private communication.
3. Reckner, L. Survey of Users of the EPA Reference Method for Measurement of Non-Methane Hydrocarbons in Ambient Air. Final Report on Contract 68-02-1206. EPA-650-75-008, Environmental Monitoring Series. Scott Environmental Technology Plumsteadville, Pennsylvania 18949. December, 1974.
4. McElroy, F. and V. Thompson. Hydrocarbon Measurement Discrepancies Among Various Analyzers Using Flame Ionization Detectors. EPA-600/4-75-010, Environmental Monitoring and Support Laboratory, Research Triangle Park, N. C. 27711. September, 1975.
5. Bruderreck, H., W. Schneider and I. Halász. Quantitative Gas Chromatographic Analysis of Hydrocarbons with Capillary Columns and Flame Ionization Detector. Analytical Chemistry 36 (3): 461-473, 1964.
6. Bocek, P., J. Novák and J. Janák. A Flame Ionization Detector for Work under Controlled Pressures. Journal of Chromtographic Science 8 (4): 226-228, 1970.
7. Littlewood, A. B. Gas Chromtography. Academic Press, New York 1970, pp. 301-307.
8. Sternberg, J. C., W. S. Gallaway and D. T. L. Jones, Gas Chromatography 1961, Lansing. N. Brenner, J. Callen, and M. Weiss, eds. Academic Press, New York, 1961, pp. 231-267.
9. McWilliam, I. G. Linearity and Response Characteristics of Flame Ionization Detector. Jour. of Chromatography 6: 110-117, 1961.
10. McWilliam, I. G. A Study of the Flame Ionization Detector. Jour. of Chromatography 51: 391-406, 1970.
11. Gill, J. M. and C. H. Hartmann. Characteristics of Ionization Detectors and Gas Chromatography Electrometers. Jour. of Gas Chromatography 5 (12): 605, 1967.
12. Lucero, D. P. and P. H. Smith. Pressurized Hydrogen Flame Ionization Detectors for Operation at Reduced Atmospheres. Jour. of Chromatographic Science 10 (9): 544-549, 1972.
13. Kauffman, H., O. Kapp, and H. Straub. A New Form of Construction for a FID. Chromtographia 5: 558-563, 1972.
14. Former, O. F. and D. J. Haase. A Statistical Study of Gas Chromatographic Systems Employing Flame Ionization Dectors. Anal. Chim. Acta. 48: 63-78, 1969.
15. Grant, D. W. and A. Clarke. A Systematic Study of the Quantitative Effect of Instrument Control on Analytical Precision in Flame Ionization Gas Chromatography. Analytical Chemistry 43 (14): 1951-1957, 1971.

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16. Cochran, W. G. and G. M. Cox. Experimental Design, 2nd Ed. John Wiley and Sons, New York, 1957.

17. Hartwell, T. Research Triangle Institute, Statistics Research Division. Private communication.

18. Valco Instruments Co. Zero-volume, switching valves; Model #LV-8-HTA.

19. Matheson Gas Products. Pneumatic flow controllers; Model 8287.

20. Supelco, Inc. Carbosieve-B (60/80 Mesh) and 10% Carbowax 20M on Supelcoport (80/100 Mesh).

21. Scott Research Laboratories, Inc. All cylinder samples except propane (NBS).

22. _______________Guidelines for Determining Performance Characteristics of Automated Methods for Measuring Nitrogen Dioxide and Hydrocarbons Corrected for Methane in Ambient Air. EPA-650/4-74-018, Environmental Monitoring Series. Quality Assurance and Environmental Monitoring Laboratory, NERC, Research Triangle Park, N. C. 27711, November, 1974.

23. David, D. J. Gas Chromatographic Detectors. John Wiley and Sons, New York, 1974, pp. 42-75.

24. Lucero, D. P. Water Vapor Sensitivity Response of Hydrogen Flame Ionization Detectors. Jour. of Chromatograph Science 10(7): 463-467, 1972.

25. Bocek, P. and J. Janak. Flame Ionization Detection. Chromatographic Reviews 15: 111-150, 1971.

26. Poli, A. A. MSA. Private communication.

27. Szepesy, L. Gas Chromatography. CRC Press, Cleveland, Ohio, 1970.

28. McNair, H. M. and E. J. Bonelli. Basic Gas Chromatography. Varian Aerograph Publications, Walnut Creek, California, 1968, p. 152.

29. Gill, J. M. Varian Aerography Previews and Reviews. Varian Aerography Publications, Walnut Creek, California, August, 1968.

30. Novak, J. Quantitative Analysis by Gas Chromatography. Marcel Dekker, Inc., New York, 1975, p. 162.

31. Ettre, L. S. Practical Gas Chromatography. Perkin Elmer Corporation, Norwalk, Connecticut, 1973, pp. 2-22.

32. Lee, J. F. and F. W. Sears. Thermodynamics, Addison-Wesley Pub. Co. Inc., Reading, Massachusetts, 1977, pp. 242-247.

33. Nelson, G. O. Controlled Test Atmospheres Principles and Techniques. Ann Arbor Science Publishers, Ann Arbor, Michigan, 1971, pp. 45-49.

34. ibid., p. 43.

35. Reschke, G. D. Optimization of a Flame Ionization Detector for Determination of Hydrocarbon in Diluted Automotive Exhausts. Paper 770141, Proceedings of the International Automotive Engineering Congress and Exposition, Cobo Hall, Detroit, February 28-March 4, 1977.

36. Black, F. and L. High. Automotive Hydrocarbon Emission Patterns and the Measurement of Non-Methane Hydrocarbon Emission Rates. Paper 770144, ibid.

37. American Society for Testing and Materials. Calibration in Air Monitoring, Proceedings of a Symposium held at the University of Colorado, Boulder, Colorado.

38. Scott, W. E. and J. T. Marrin. Problems with Zero Gases for Ultra-Low Level Measurements of Air Pollutants. pp. 275-281 in Ref. 37.

39. Wechter, S. G. and H. A. Greico. Gas Standards, How Standard are They? pp. 246-254 in Ref. 37.

40. Dieck, R. H. Gas Turbine Emission Measurement Instrument Calibration. pp. 16-39 in Ref. 37.

## APPENDIX A

## FID AND GC STATISTICAL TEST PLANS AND RESULTS

The flame ionization detector was evaluated for the effect of six variables at five levels. The variables and levels are shown below in Table 24. The test plan included 65 observations at various combinations of levels that were based on a modified fractional factorial design. The test plan is given in Table 25.

TABLE 24. TEST VARIABLES AND LEVELS FOR FID EVALUATION

| VARIABLES | | LEVELS | | | | |
|---|---|---|---|---|---|---|
| | | -2 | -1 | 0 | 1 | 2 |
| $H_2$ Flow ($cm^3$/min) | $X_1$ | 21 | 28 | 35 | 42 | 49 |
| Air Flow ($cm^3$/min) | $X_2$ | 200 | 267 | 333 | 400 | 467 |
| Carrier Air Flow ($cm^3$/min) | $X_3$ | 15 | 25 | 35 | 45 | 55 |
| Voltage (volts) | $X_4$ | 50 | 100 | 150 | 200 | 250 |
| Pressure (torr) | $X_5$ | 740 | 750 | 760 | 770 | 780 |
| Sample Size (ppm $CH_4$) | $X_6$ | 2<br>(0.2 ppm) | 4<br>(0.5 ppm) | 6<br>(1 ppm) | 8<br>(1.5 ppm) | 10<br>(2 ppm) |

The analysis program for this test plan included provision for the fact that test variables might not be precisely at the indicated levels. This made the actual setting of variables for each observation easier and facilitated the experiments. The actual (coded) values used for each observation are shown in Table 26 along with the response (last colum of data) in coded units of FID current that resulted for each combination of variables at the given level.

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## TABLE 25. TEST PLAN FOR FID EVALUATION

| Run | $H_2$ Flow $X_1$ | Air Flow $X_2$ | Carrier Air Flow $X_3$ | Voltage $X_4$ | Pressure $X_5$ | Sample Size $X_6$ |
|---|---|---|---|---|---|---|
| 1 | -1 (28) | -1 (267) | -1 (25) | -1 (100) | -1 (750) | -1 (4) |
| 2 | 1 (42) | -1 | -1 | 1 (200) | -1 | -1 |
| 3 | 1 | 1 (400) | -1 | -1 | -1 | -1 |
| 4 | -1 | 1 | -1 | 1 | -1 | -1 |
| 5 | 1 | -1 | 1 (45) | -1 | -1 | -1 |
| 6 | -1 | -1 | 1 | 1 | -1 | -1 |
| 7 | -1 | 1 | 1 | -1 | -1 | -1 |
| 8 | 1 | 1 | 1 | 1 | -1 | -1 |
| 9 | 1 | -1 | -1 | -1 | 1 (770) | -1 |
| 10 | -1 | -1 | -1 | 1 | 1 | -1 |
| 11 | -1 | 1 | -1 | -1 | 1 | -1 |
| 12 | 1 | 1 | -1 | 1 | 1 | -1 |
| 13 | -1 | -1 | 1 | -1 | 1 | -1 |
| 14 | 1 | -1 | 1 | 1 | 1 | -1 |
| 15 | 1 | 1 | 1 | -1 | 1 | -1 |
| 16 | -1 | 1 | 1 | 1 | 1 | -1 |
| 17 | 1 | -1 | -1 | -1 | -1 | 1 (8) |
| 18 | -1 | -1 | -1 | 1 | -1 | 1 |
| 19 | -1 | 1 | -1 | -1 | -1 | 1 |
| 20 | 1 | 1 | -1 | 1 | -1 | 1 |
| 21 | -1 | -1 | 1 | -1 | -1 | 1 |
| 22 | 1 | -1 | 1 | 1 | -1 | 1 |
| 23 | 1 | 1 | 1 | -1 | -1 | 1 |
| 24 | -1 | 1 | 1 | 1 | -1 | 1 |
| 25 | -1 | -1 | -1 | -1 | 1 | 1 |
| 26 | 1 | -1 | -1 | 1 | 1 | 1 |
| 27 | 1 | 1 | -1 | -1 | 1 | 1 |
| 28 | -1 | 1 | -1 | 1 | 1 | 1 |
| 29 | 1 | -1 | 1 | 1 | 1 | 1 |
| 30 | -1 | -1 | 1 | 1 | 1 | 1 |

TABLE 25. (Continued)

| Run | $H_2$ Flow $X_1$ | Air Flow $X_2$ | Carrier Air Flow $X_3$ | Voltage $X_4$ | Pressure $X_5$ | Sample Size $X_6$ |
|---|---|---|---|---|---|---|
| 31 | -1 | -1 | 1 | -1 | 1 | 1 |
| 32 | 1 | 1 | 1 | 1 | 1 | 1 |
| 33 | 0 (35) | 0 (333) | 0 (35) | 0 (150) | 0 (760) | 0 (6) |
| 34 | 0 | 0 | 0 | 0 | 0 | 0 |
| 35 | 0 | 0 | 0 | 0 | 0 | 0 |
| 36 | 0 | 0 | 0 | 0 | 0 | 0 |
| 37 | 0 | 0 | 0 | 0 | 0 | 0 |
| 38 | 0 | 0 | 0 | 0 | 0 | 0 |
| 39 | 0 | 0 | 0 | 0 | 0 | 0 |
| 40 | 0 | 0 | 0 | 0 | 0 | 0 |
| 41 | 0 | 0 | 0 | 0 | 0 | 0 |
| 42 | -2 (21) | 0 | 0 | 0 | 0 | 0 |
| 43 | -2 | 0 | 0 | 0 | 0 | 0 |
| 44 | 2 (49) | 0 | 0 | 0 | 0 | 0 |
| 45 | 2 | 0 | 0 | 0 | 0 | 0 |
| 46 | 0 | -2 (200) | 0 | 0 | 0 | 0 |
| 47 | 0 | -2 | 0 | 0 | 0 | 0 |
| 48 | 0 | 2 (467) | 0 | 0 | 0 | 0 |
| 49 | 0 | 2 | 0 | 0 | 0 | 0 |
| 50 | 0 | 0 | -2 (15) | 0 | 0 | 0 |
| 51 | 0 | 0 | -2 | 0 | 0 | 0 |
| 52 | 0 | 0 | 2 (55) | 0 | 0 | 0 |
| 53 | 0 | 0 | 2 | 0 | 0 | 0 |
| 54 | 0 | 0 | 0 | -2 (50) | 0 | 0 |
| 55 | 0 | 0 | 0 | -2 | 0 | 0 |
| 56 | 0 | 0 | 0 | 2 (250) | 0 | 0 |
| 57 | 0 | 0 | 0 | 2 | 0 | 0 |
| 58 | 0 | 0 | 0 | 0 | -2 (740) | 0 |
| 59 | 0 | 0 | 0 | 0 | -2 | 0 |
| 60 | 0 | 0 | 0 | 0 | 2 (780) | 0 |

TABLE 25. (Continued)

| Run | $H_2$ Flow $X_1$ | Air Flow $X_2$ | Carrier Air Flow $X_3$ | Voltage $X_4$ | Pressure $X_5$ | Sample Size $X_6$ |
|---|---|---|---|---|---|---|
| 61 | 0 | 0 | 0 | 0 | 2 | 0 |
| 62 | 0 | 0 | 0 | 0 | 0 | -2 (2) |
| 63 | 0 | 0 | 0 | 0 | 0 | -2 |
| 64 | 0 | 0 | 0 | 0 | 0 | 2 (10) |
| 65 | 0 | 0 | 0 | 0 | 0 | 2 |

## TABLE 26. STATISTICAL ANALYSIS RESULTS

| OBS | X1 | X2 | X3 | X4 | X5 | X6 | RES |
|---|---|---|---|---|---|---|---|
| 1 | -0.98571 | -0.99850 | -1.00 | -1 | -1.0 | -1 | 17.8 |
| 2 | 1.25714 | -0.98045 | -1.00 | 1 | -1.0 | -1 | 53.2 |
| 3 | 1.05714 | 0.96541 | -1.00 | -1 | -1.0 | -1 | 65.5 |
| 4 | -1.50000 | 1.00000 | -1.00 | 1 | -1.0 | -1 | 62.8 |
| 5 | 1.10000 | -0.98647 | 0.94 | -1 | -1.0 | -1 | 120.0 |
| 6 | -0.94286 | -1.03308 | 0.89 | 1 | -1.0 | -1 | 110.4 |
| 7 | -1.01429 | 1.03759 | 1.08 | -1 | -1.0 | -1 | 112.5 |
| 8 | 0.98571 | 0.95789 | 0.97 | 1 | -1.0 | -1 | 133.2 |
| 9 | 1.42857 | -1.07519 | -1.00 | -1 | 1.0 | -1 | 49.2 |
| 10 | -1.04286 | -1.00000 | -1.01 | 1 | 1.0 | -1 | 55.3 |
| 11 | -0.95714 | 1.00000 | -1.02 | -1 | 1.0 | -1 | 56.0 |
| 12 | 1.18571 | 1.00000 | -1.02 | 1 | 1.0 | -1 | 37.6 |
| 13 | -0.98571 | -1.02556 | 1.06 | -1 | 1.0 | -1 | 121.5 |
| 14 | 1.05714 | -1.00602 | 1.05 | 1 | 1.0 | -1 | 123.0 |
| 15 | 1.05714 | 1.06466 | 1.01 | -1 | 1.0 | -1 | 120.0 |
| 16 | -1.00000 | 1.04812 | 0.99 | 1 | 1.0 | -1 | 118.5 |
| 17 | 0.95714 | -1.03008 | -1.02 | -1 | -1.0 | 1 | 105.0 |
| 18 | -0.95714 | -0.99098 | -1.01 | 1 | -1.0 | 1 | 135.0 |
| 19 | -0.98571 | 0.96992 | -1.02 | -1 | -1.0 | 1 | 130.5 |
| 20 | 0.97143 | 0.97444 | -1.00 | 1 | -1.0 | 1 | 106.5 |
| 21 | -1.02857 | -0.98797 | 1.04 | -1 | -1.0 | 1 | 300.0 |
| 22 | 0.94286 | -0.99248 | 1.01 | 1 | -1.0 | 1 | 315.0 |
| 23 | 0.98571 | 1.01203 | 1.01 | -1 | -1.0 | 1 | 343.0 |
| 24 | -0.94286 | 0.98797 | 0.98 | 1 | -1.0 | 1 | 297.0 |
| 25 | -0.94286 | -0.99248 | -1.00 | -1 | 1.0 | 1 | 140.0 |
| 26 | 0.98571 | -0.98346 | -0.99 | 1 | 1.0 | 1 | 104.0 |
| 27 | 1.02857 | 0.97143 | -1.02 | -1 | 1.0 | 1 | 98.0 |
| 28 | -0.98571 | 1.02105 | -1.00 | 1 | 1.0 | 1 | 153.0 |
| 29 | 1.05714 | -0.99248 | 1.01 | -1 | 1.0 | 1 | 305.0 |
| 30 | -0.95714 | -1.00000 | 0.94 | 1 | 1.0 | 1 | 300.0 |
| 31 | -0.97143 | 0.98947 | 1.00 | -1 | 1.0 | 1 | 296.0 |
| 32 | 0.95714 | 1.01654 | 1.00 | 1 | 1.0 | 1 | 297.0 |
| 33 | -0.28571 | 0.02256 | 0.10 | 0 | 0.0 | 0 | 177.0 |
| 34 | -0.21429 | 0.06165 | -0.07 | 0 | 0.0 | 0 | 156.0 |
| 35 | -0.04286 | -0.05263 | 0.02 | 0 | 0.0 | 0 | 159.0 |
| 36 | -0.42857 | -0.00752 | 0.00 | 0 | 0.0 | 0 | 160.0 |
| 37 | -0.25714 | -0.02256 | 0.03 | 0 | 0.0 | 0 | 156.0 |
| 38 | 0.41429 | -0.12782 | -0.06 | 0 | 0.0 | 0 | 150.0 |
| 39 | 0.01429 | -0.01353 | 0.00 | 0 | 0.0 | 0 | 151.5 |
| 40 | 0.01429 | -0.00752 | 0.01 | 0 | 0.0 | 0 | 151.5 |
| 41 | 0.02857 | -0.00752 | 0.01 | 0 | 0.0 | 0 | 151.0 |
| 42 | -1.95714 | -0.00451 | 0.01 | 0 | 0.0 | 0 | 157.5 |
| 43 | -1.97143 | -0.00752 | 0.02 | 0 | 0.0 | 0 | 154.5 |
| 44 | 1.97143 | -0.00752 | 0.02 | 0 | 0.0 | 0 | 127.5 |
| 45 | 2.07143 | -0.01955 | 0.00 | 0 | 0.0 | 0 | 127.5 |
| 46 | -0.02857 | -2.00752 | 0.00 | 0 | 0.0 | 0 | 150.0 |
| 47 | -0.02857 | -1.98496 | 0.01 | 0 | -0.8 | 0 | 165.0 |
| 48 | 0.00000 | 1.99098 | -0.02 | 0 | -0.8 | 0 | 148.5 |
| 49 | 0.00000 | 1.97744 | 0.01 | 0 | -0.8 | 0 | 150.0 |
| 50 | 0.05714 | -0.03759 | -1.96 | 0 | -0.8 | 0 | 34.0 |
| 51 | 0.15714 | 0.06617 | -1.94 | 0 | -0.8 | 0 | 30.3 |
| 52 | 0.11429 | -0.00752 | 1.93 | 0 | -0.8 | 0 | 271.5 |
| 53 | 0.28571 | -0.03759 | 1.95 | 0 | -0.8 | 0 | 271.5 |
| 54 | 0.07143 | -0.00752 | -0.07 | -2 | -0.8 | 0 | 165.0 |
| 55 | -0.05714 | 0.07669 | 0.00 | -2 | -0.8 | 0 | 166.5 |

TABLE 26. (Continued)

| OBS | X1 | X2 | X3 | X4 | X5 | X6 | RES |
|---|---|---|---|---|---|---|---|
| 56 | -.085714 | .0812030 | -.01 | 2 | -0.8 | 0 | 169.5 |
| 57 | .242857 | -.0766917 | -.01 | 2 | -0.8 | 0 | 166.5 |
| 58 | .271429 | .0827068 | .00 | 0 | -4.0 | 0 | 166.5 |
| 59 | -.200000 | -.0075188 | -.03 | 0 | -4.0 | 0 | 172.5 |
| 60 | .357143 | .0526316 | -.03 | 0 | 2.0 | 0 | 160.5 |
| 61 | .357143 | -.0526316 | .00 | 0 | 2.0 | 0 | 162.0 |
| 62 | -.185714 | -.0616541 | .19 | 0 | 0.0 | -2 | 19.0 |
| 63 | -.885714 | -.0526316 | .14 | 0 | 0.0 | 2 | 333.0 |
| 64 | -.314286 | -.0075188 | .35 | 0 | 0.0 | 2 | 360.0 |

The coded variables in Table 26 can be translated to measured laboratory values by using the relations

$$H_2\ \text{Flow}\ (\text{cm}^3/\text{min}) = 7\ X_1 + 35 \tag{23}$$

$$\text{Support Air Flow}\ (\text{cm}^3/\text{min}) = 66.5\ X_2 + 333.5 \tag{24}$$

$$\text{Carrier Air Flow}\ (\text{cm}^3/\text{min}) = 10\ X_3 + 35 \tag{25}$$

$$\text{Electrode Potential (Volts)} = 50\ X_4 + 150 \tag{26}$$

$$\text{Pressure (torr)} = 10\ X_5 + 760 \tag{27}$$

The sample size in ppm $CH_4$ was as shown in Table 24, ranging from 0.2 ppm to 2 ppm. The response values shown in Table 26 were related to the FID signal current by multiplication by a conversion factor of $7.87 \times 10^{-14}$ Ampere.

An example of conversion from the coded values of Table 26 to experimental values is provided by considering observation number 23. An FID signal current of $2.7 \times 10^{-11}$ amperes resulted when 1.5 ppm methane was injected (from a 3 $cm^3$ sample volume) into the FID operated at 750 torr pressure, with an electrode potential of 100 volts. The hydrogen fuel flow rate was 41.9 $cm^3$/min, the carrier air flow rate was 45.1 $cm^3$/min and the support air flow rate was 400.8 $cm^3$/min.

The mean values of response for the variables at each level were as shown in Figures 10 through 15 in Section 4.

The coded variable values $X_1$ through $X_6$ and RES for each of the 64 observations were used as inputs to a statistical analysis program REGR of the STATISTICAL ANALYSIS SYSTEM authored by A. J. Barr and J. H. Goodnight of the N. C. State University Institute of Statistics. This program is in the library of routines available at The Universities Computing Center (TUCC), Research Triangle Park, N. C.

The output of the program gave an analysis of variance table and related statistical measures for the dependent variable RES and each of the independent variables used in the model. The first trial used 27 independent variables, $X_1$ through $X_6$, their squares and cross products. In addition the program gave coefficient values ("B values") for the regression model, of the form

$$RES = B_o \sum_{n=1}^{6} B_n X_n + \sum_{i,j=1}^{6} B_{ij} X_i X_j \; . \qquad (28)$$

Goodness of fit was measured by the square of the multiple correlation coefficient, "R-square", and the coefficient of variability, "C.V.", expressed as a percent.

The full model had an R-square value of 0.989567 and a C.V. of 7.3%. Upon examination of the statistical measures of significance for the independent variables it was apparent that many could be discarded as having negligible effect on the model. A second model, retaining only the independent variables $X_1$, $X_3$, $X_6$, $X_1X_3$, $X_1X_5$, $X_1X_6$, $X_2X_5$, $X_3X_6$, $X_1X_1$ and $X_3X_3$, was tested. The R-square value for this was 0.985352 and the C.V. was 7.13%. The mathematical expression for this model is given in equation (1) in Section 4 of this report.

A final trial was made using the variables $X_3$, $X_6$ and $X_3X_6$. The R-square value for this was 0.972016 and the C.V. increased to 9.26%. This still appears to be a reasonable fit to the data. The mathematical form for this simpler model is given in equation (7) in Section 4.

The results of the modeling of the response surface may be interpreted as follows. To a good approximation the FID response to methane over the range of 0.2 to 2 ppm is dependent only upon the methane concentration and the carrier air flow. The next higher level of modeling takes into account the effect of hydrogen flow as well and the interactions between $H_2$ and carrier air flow rates, $H_2$ and sample size and carrier air flow and sample size. There is also a slight effect of pressure but this is not as significant as the other factors.

These results and the use of the mathematical model for sensitivity analyses are discussed in Section 4.

As was discussed in Section 4, the statistical analysis indicated that the hydrogen flow and carrier air flow rates were the most influential operating variables for a given sample sign. Accordingly, when the FID was installed in the RTI-designed gas chromatographic (GC) analyzer, a simpler test design employing only three variables at three levels was used to obtain optimum flow setting data. The variables and levels are given in Table 27 below. The sample size used in all observations was 2 $cm^3$ of 2.05 ppm $CH_4$ in air, and a temperature of about 87°C was used.

TABLE 27. TEST VARIABLES AND LEVELS FOR FID-GC EVALUATION

| VARIABLES | LEVELS | | |
|---|---|---|---|
| | -1 | 0 | 1 |
| Hydrogen Flow Rate ($cm^3$/min) | 20 | 32 | 42 |
| Carrier Air Flow Rate ($cm^3$/min) | 30 | 40 | 50 |
| Support Air Flow Rate ($cm^3$/min) | 100 | 200 | 300 |

The test plan and resulting response values are given in Table 28. Mean values of response were as plotted in Figure 18 of Section 5. The "response number" values in Table 28 can be converted to FID signal current values by multiplying by $7.87 \times 10^{-14}$ Ampere.

Because of the fewer number of variables and the experience with the FID evaluation no regression model was used to analyze the data.

**TABLE 28. DESIGN OF GC EVALUATION TEST AND RESULTING RESPONSES**

| $H_2$ Flow | Carrier Air | Support Air | Response No. |
|---|---|---|---|
| -1 | 0 | 0 | 114.7 |
| -1 | 0 | 1 | 106.6 |
| -1 | 0 | -1 | 109.8 |
| -1 | 1 | 0 | 78.5 |
| -1 | 1 | 1 | 77.0 |
| -1 | 1 | -1 | 77.3 |
| -1 | -1 | 0 | 123.2 |
| -1 | -1 | 1 | 120.9 |
| -1 | -1 | -1 | 128.4 |
| 0 | 0 | 0 | 188.6 |
| 0 | 0 | 1 | 184.9 |
| 0 | 0 | -1 | 189.0 |
| 0 | 1 | 0 | 194.6 |
| 0 | 1 | 1 | 189.3 |
| 0 | 1 | -1 | 187.0 |
| 0 | -1 | 0 | 156.6 |
| 0 | -1 | 1 | 153.0 |
| 0 | -1 | -1 | 154.1 |
| 1 | 0 | 0 | 199.9 |
| 1 | 0 | 1 | 197.3 |
| 1 | 0 | -1 | 187.5 |
| 1 | 1 | 0 | 231.0 |
| 1 | 1 | 1 | 230.2 |
| 1 | 1 | -1 | 216.0 |
| 1 | -1 | 0 | 143.8 |
| 1 | -1 | 1 | 139.5 |
| 1 | -1 | -1 | 135 |

# APPENDIX B

## COMPARATIVE EVALUATION DATA

Instruments zero points were set with air containing less than 50 ppb THC and span was set with 8 ppm $CH_4$ in air to begin calibration stability tests on July 28, 1976. These tests continued until August 16, 1976. During this period precision was measured daily by repetitive injections of methane, approximately 2.2 ppm in air for the $CH_4$ channel, and 0.53 ppm propylene plus 2.2 ppm methane in air for the THC channel.

Plots of mean zero drift and standard deviation on a 24-hour basis are shown in Figures 35 through 44.

Span drift data is presented in Section 7, Table 12.

Precision data as standard deviations of response to repeated injections over a four-to-seven hour period daily have been presented in Section 7, Table 13.

The NMHC response under various conditions was presented in Section 7, Tables 14 through 21.

Ambient air data from the comparative evaluation over the period 1600 August 28, 1976 through 1500 August 31, 1976 are given in Table 29. Using hourly averages at increments of two hours, these data were used to calculate the mean $CH_4$ and the ratio of individual instrument values to the mean value. These data are presented in Table 30. Similar data for THC readings are given in Table 31.

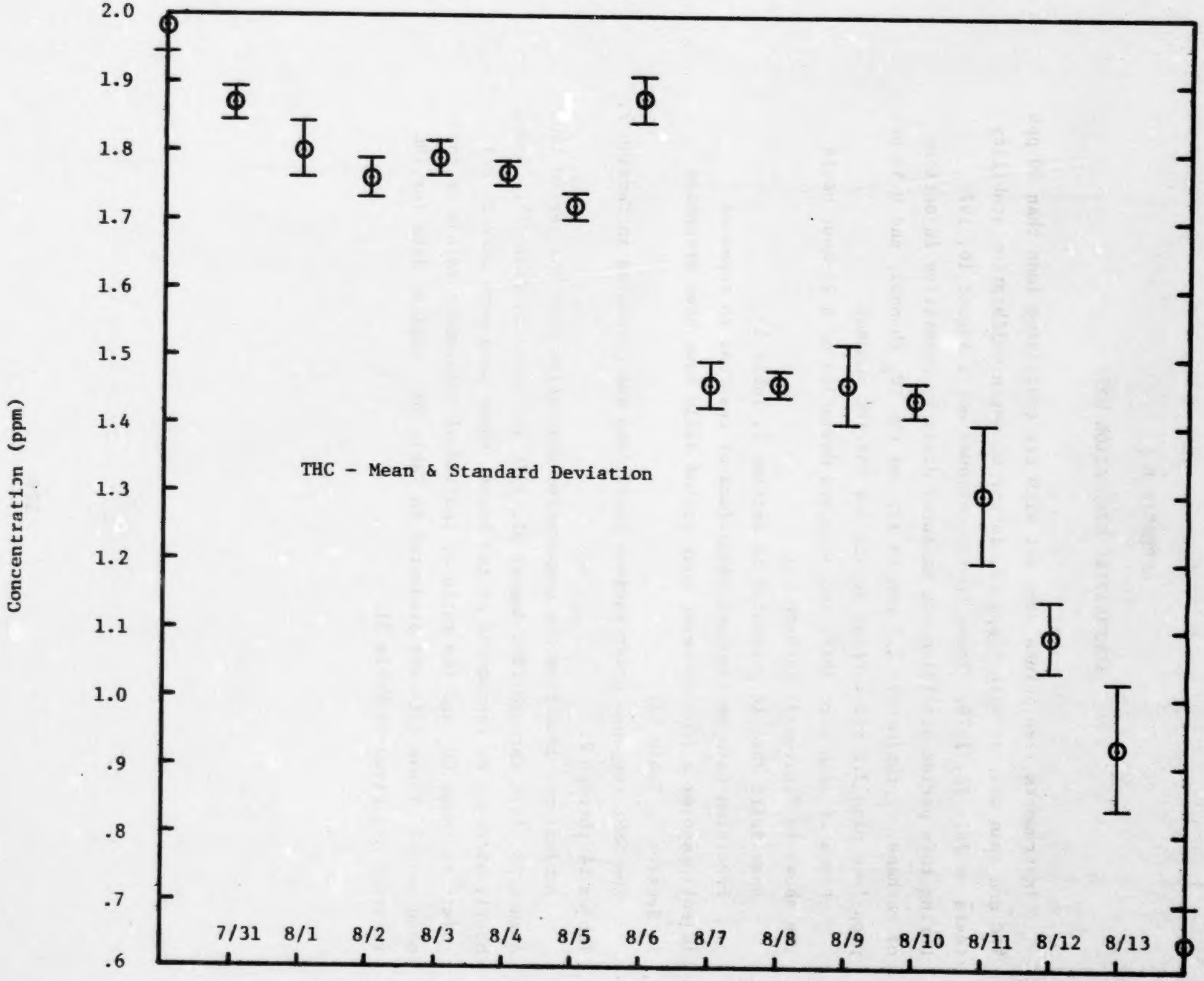

Figure 35. Mean and standard deviation of total hydrocarbon indication of zero air for each twenty-four hour period of long term stability test;

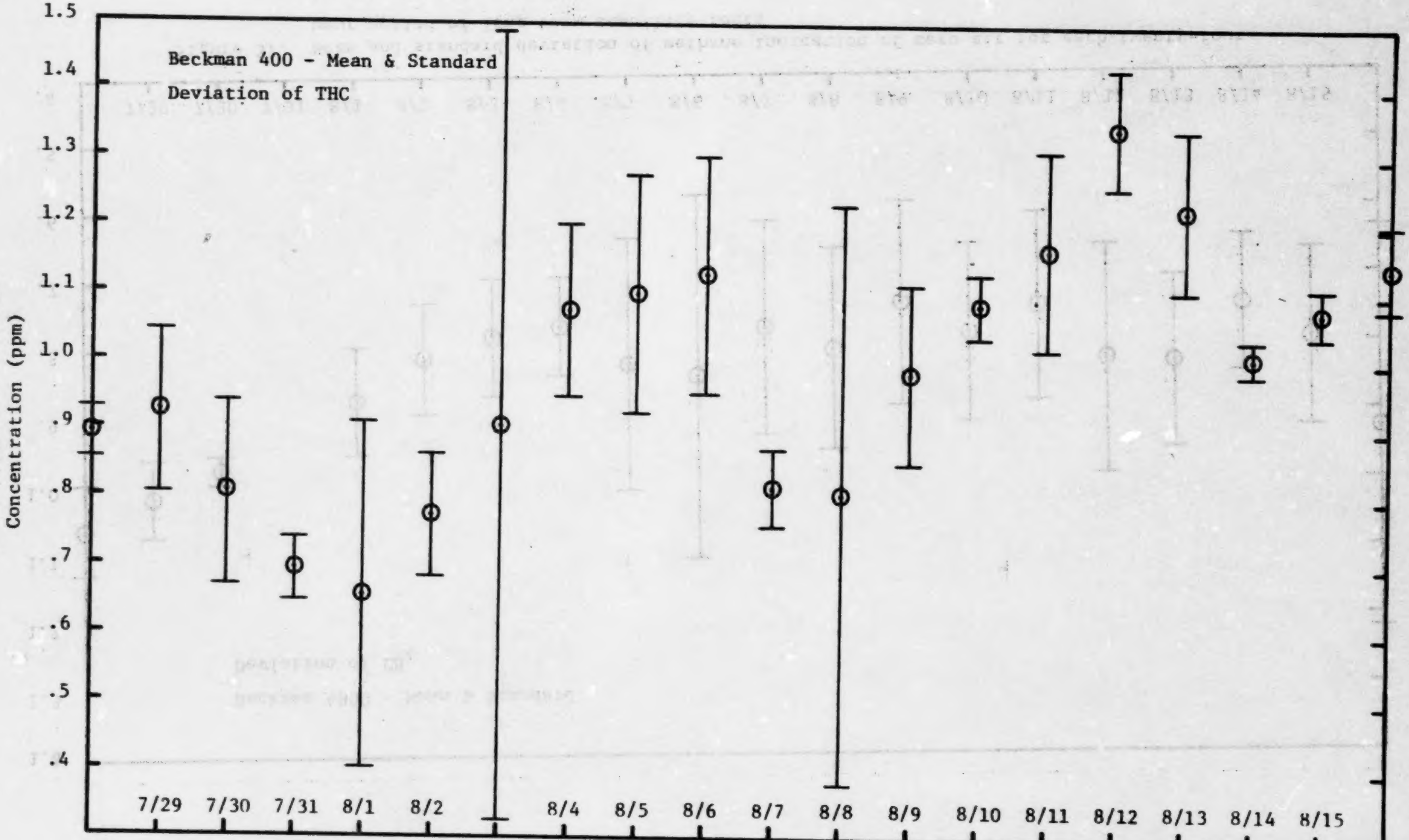

Figure 36. Mean and standard deviation of total hydrocarbon indication of zero air for each twenty-four hour period of long term stability test;

Instrument: Beckman 400.

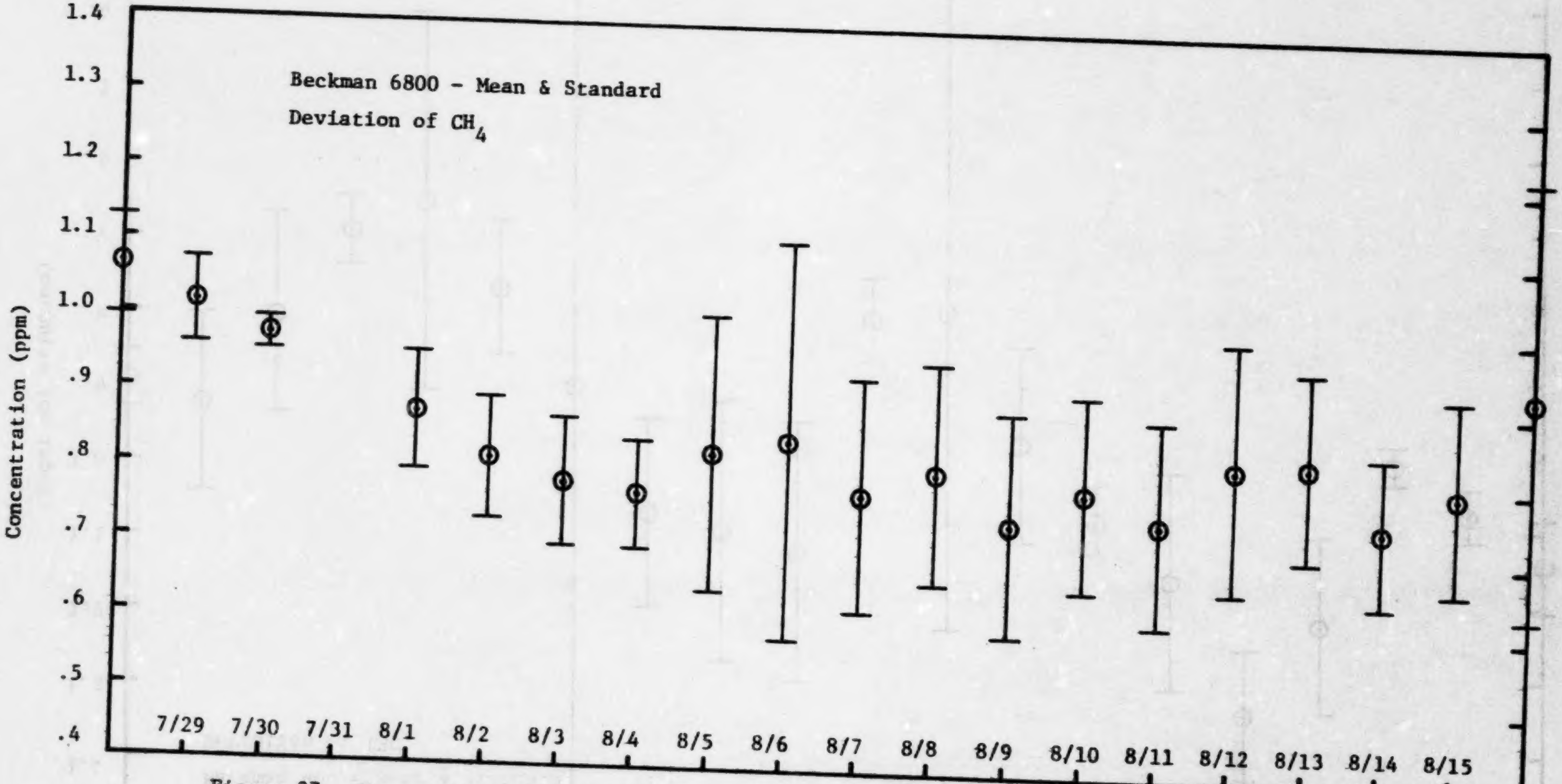

Figure 37. Mean and standard deviation of methane indication of zero air for each twenty-four hour period of long term stability test;
Instrument: Beckman 6800

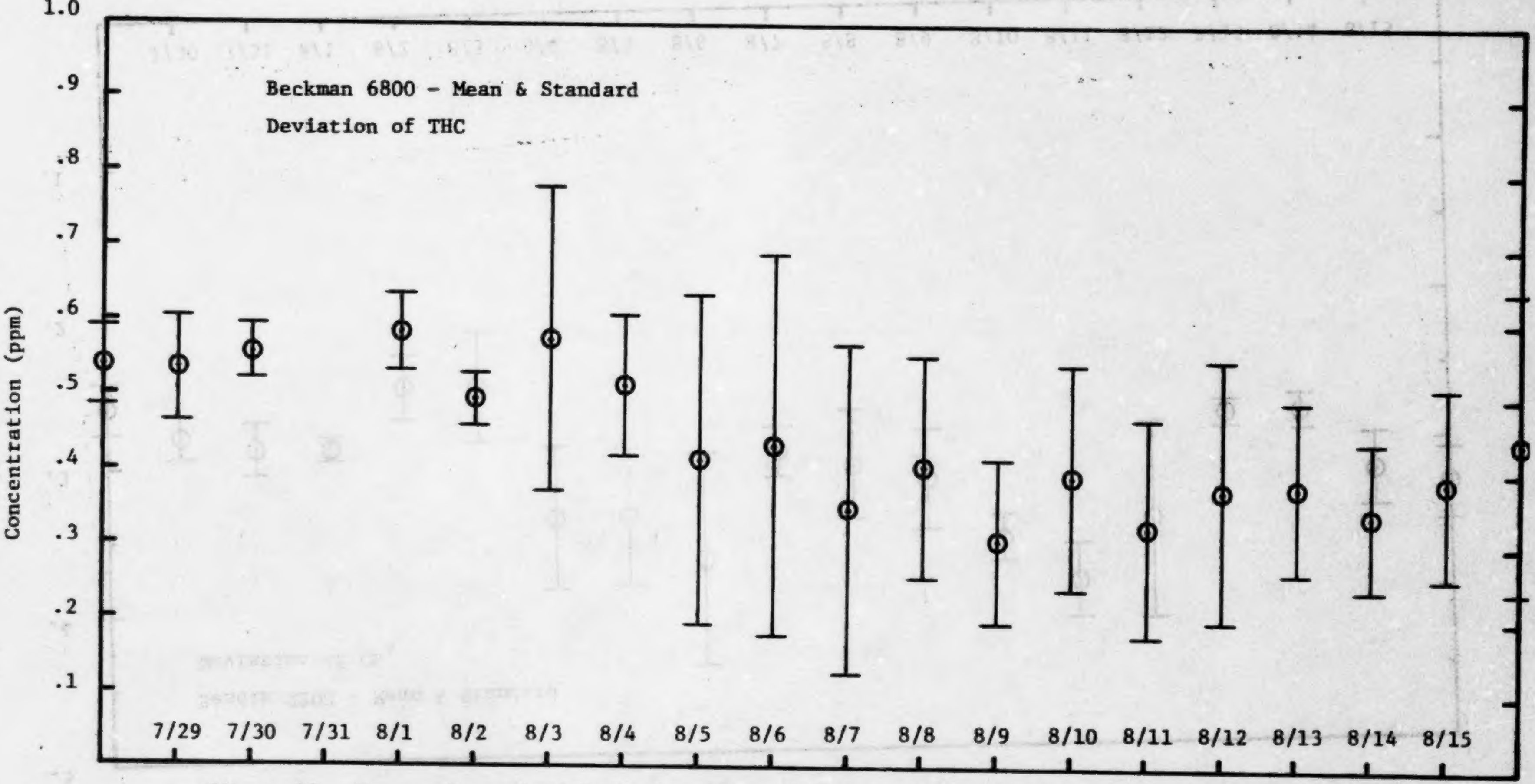

Figure 38. Mean and standard deviation of total hydrocarbon indication of zero air for each twenty-four hour period of long term stability test;

Instrument: Beckman 6800.

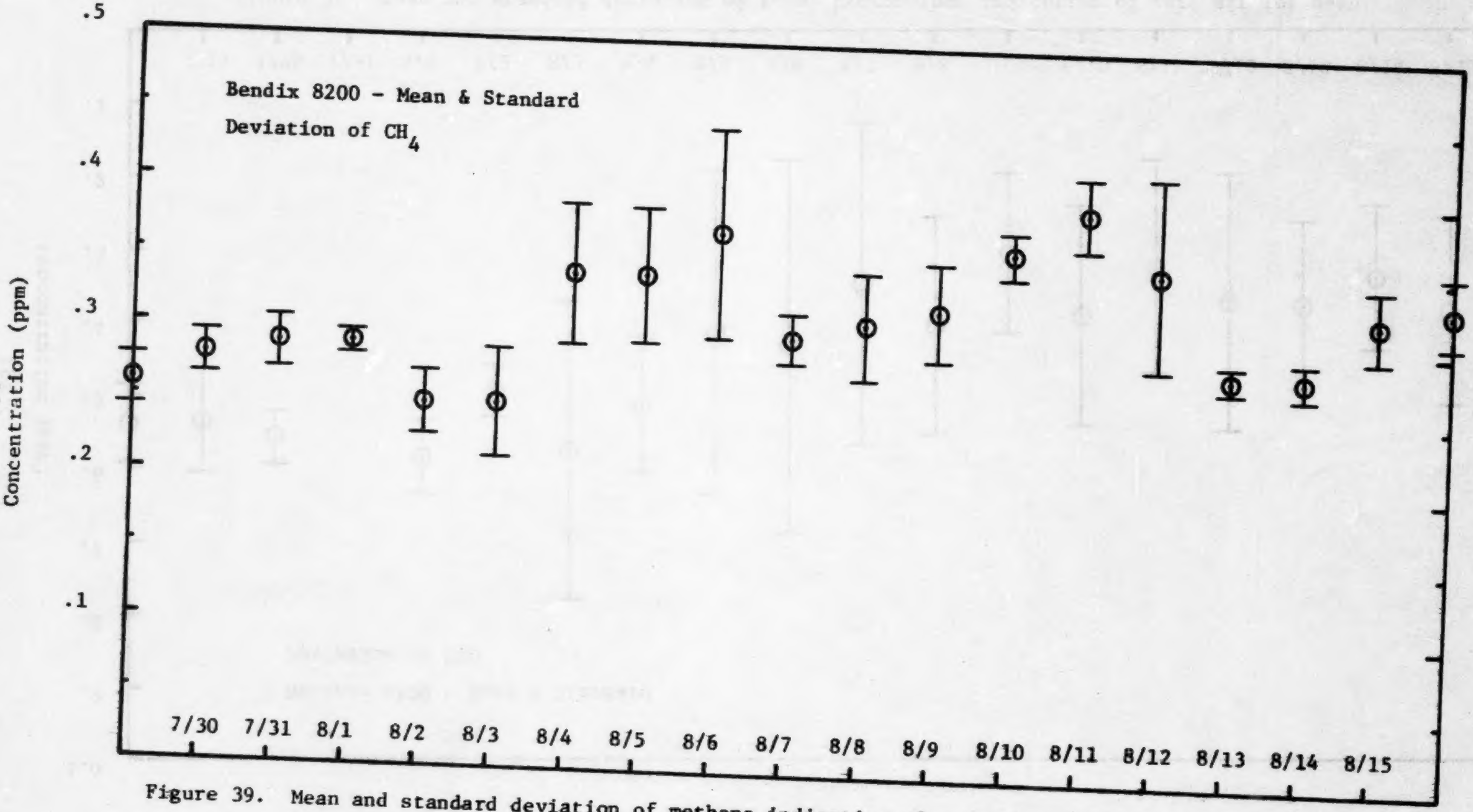

Figure 39. Mean and standard deviation of methane indication of zero air for each twenty-four hour period of long term stability test;

Instrument: Bendix 8200.

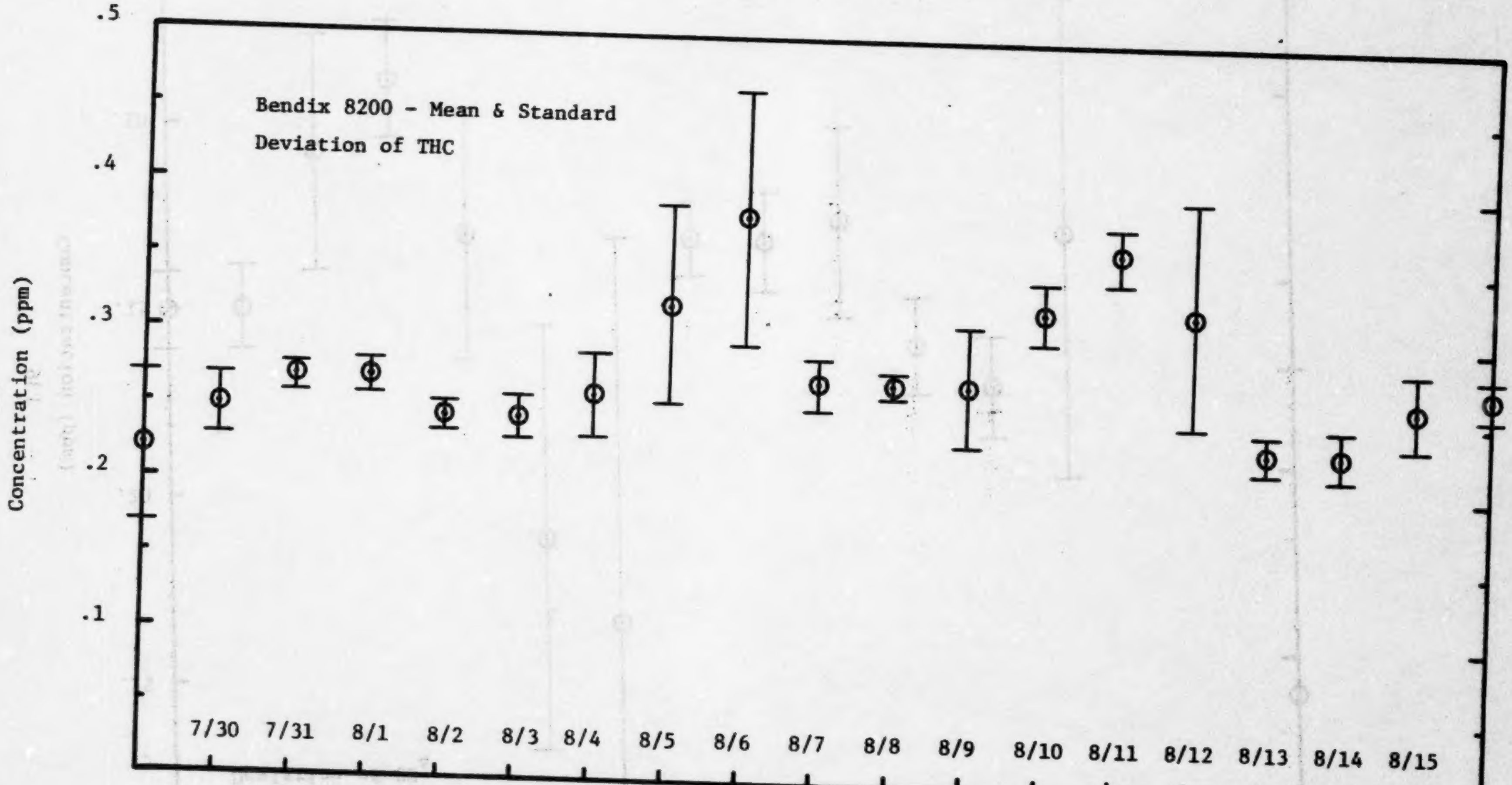

Figure 40. Mean and standard deviation of total hydrocarbon indication of zero air for each twenty-four hour period of long term stability test;

Instrument: Bendix 8200.

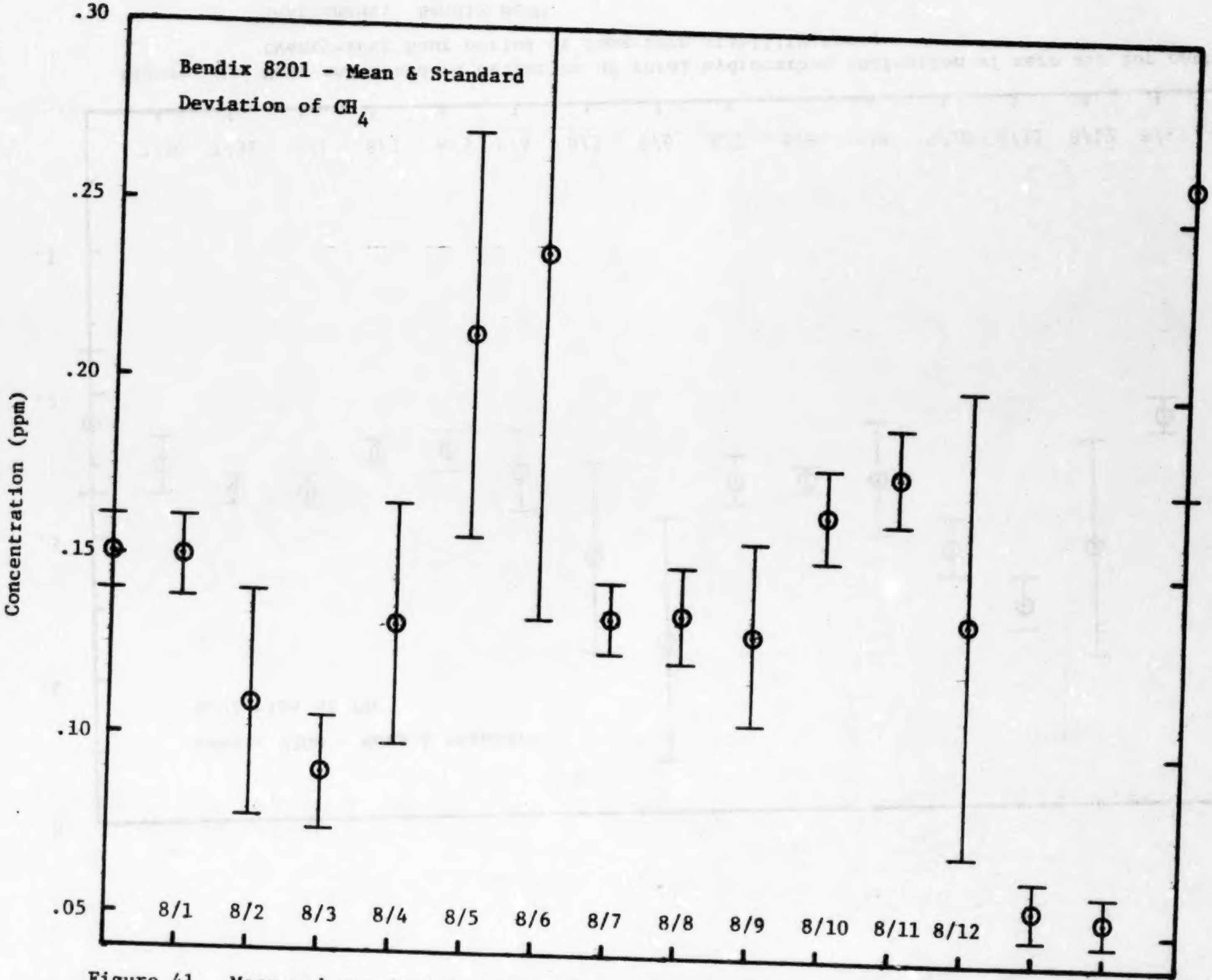

Figure 41. Mean and standard deviation of methane indication of zero air for each twenty-four hour period of long term stability test; Instrument: Bendix

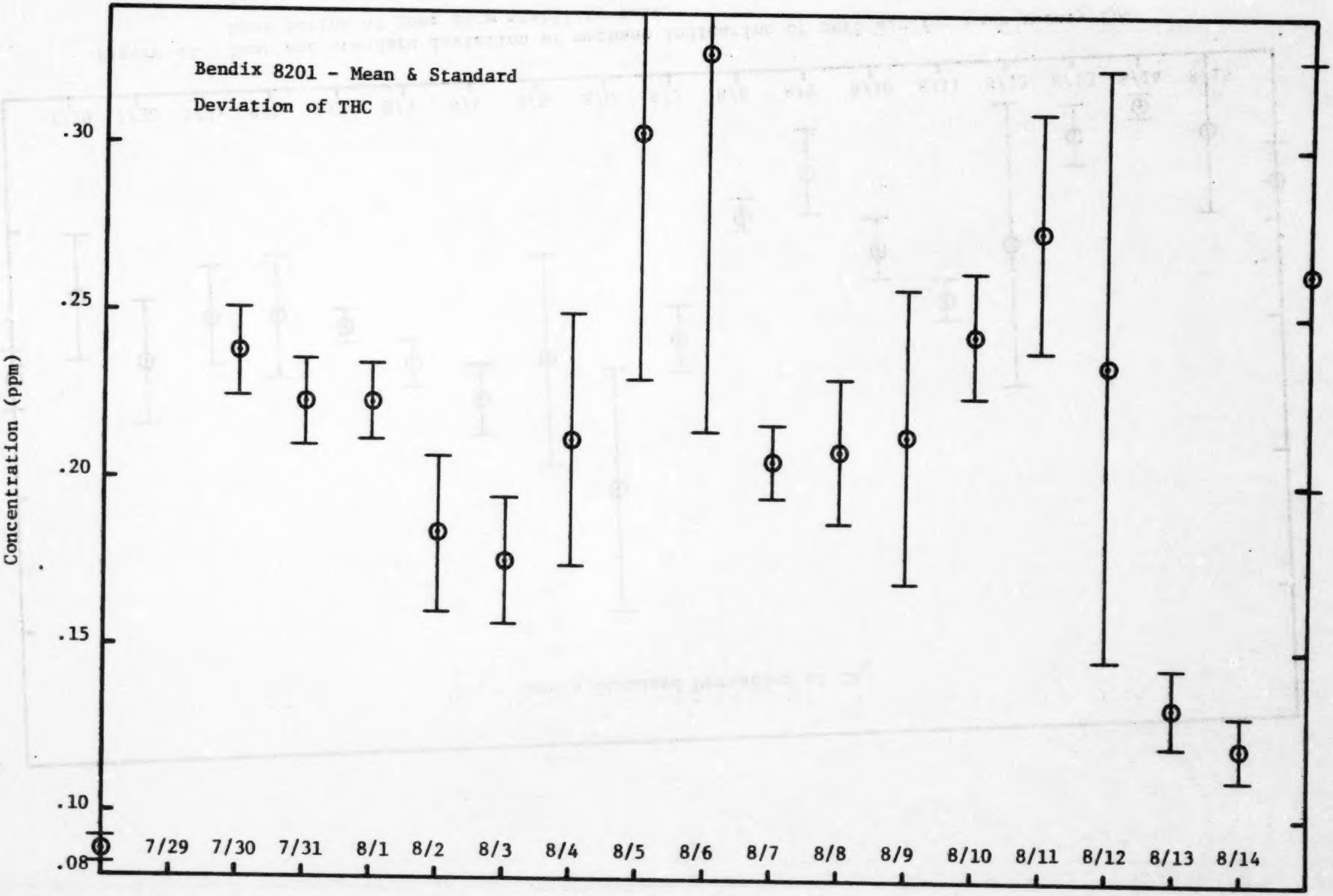

Figure 42. Mean and standard deviation of total hydrocarbon indication of zero air for each twenty-four hour period of long term stability test;

Instrument: Bendix 8201.

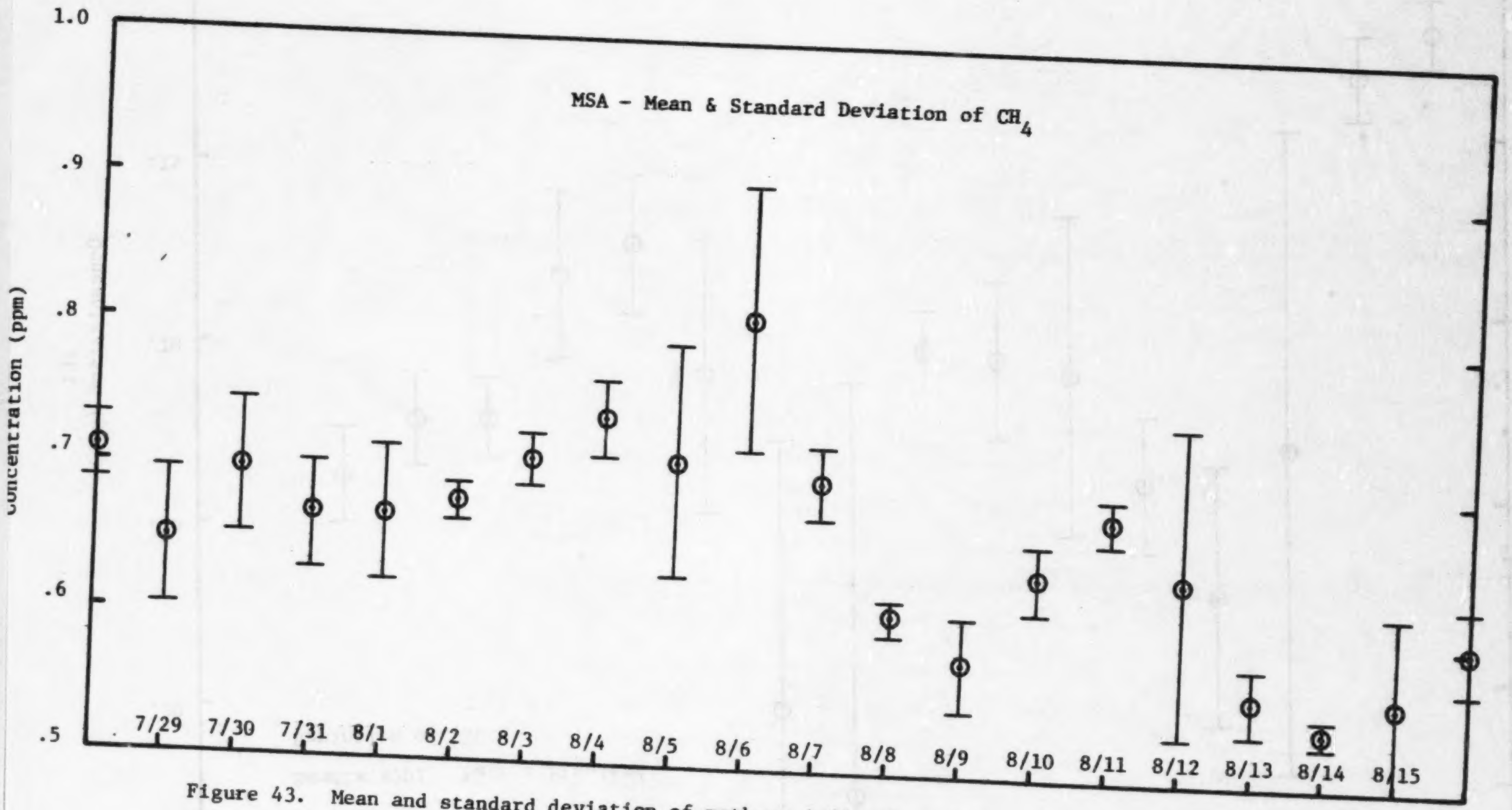

Figure 43. Mean and standard deviation of methane indication of zero air for each twenty-four hour period of long term stability test;

Instrument: MSA 11-2.

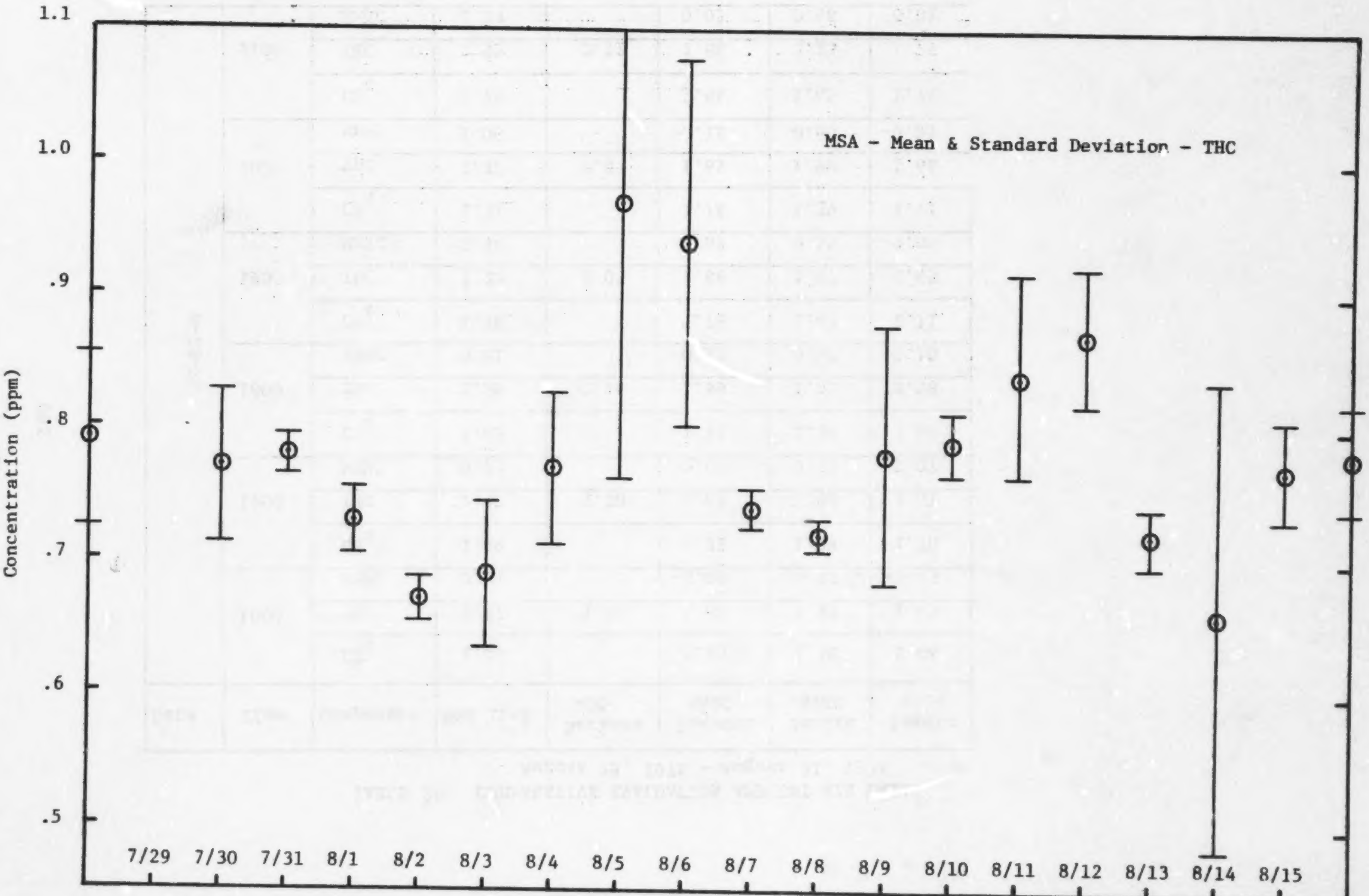

Figure 44. Mean and standard deviation of total hydrocarbon indication of zero air for each twenty-four hour period of long term stability test;

Instrument: MSA 11-2.

TABLE 29. COMPARATIVE EVALUATION AMBIENT AIR DATA.
August 28, 1976 - August 31, 1976

| Date | Time | Component | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
|---|---|---|---|---|---|---|---|
| 8-28-76 | 1600 | $CH_4$ | 1.46 |  | 1.70 | 1.38 | 1.66 |
|  |  | THC | 2.37 | 1.98 | 1.62 | 1.95 | 1.63 |
|  |  | NMHC | 0.91 |  | -0.08 | 0.57 | -0.03 |
|  | 1700 | $CH_4$ | 1.49 |  | 1.72 | 1.39 | 1.70 |
|  |  | THC | 2.32 | 2.20 | 1.65 | 1.92 | 1.61 |
|  |  | NMHC | 0.83 |  | -0.07 | 0.53 | -0.07 |
|  | 1800 | $CH_4$ | 1.45 |  | 1.71 | 1.39 | 1.68 |
|  |  | THC | 2.26 | 2.16 | 1.59 | 1.91 | 1.58 |
|  |  | NMHC | 0.81 |  | -0.12 | 0.52 | -0.10 |
|  | 1900 | $CH_4$ | 1.38 |  | 1.76 | 1.42 | 1.71 |
|  |  | THC | 2.32 | 2.05 | 1.68 | 1.97 | 1.63 |
|  |  | NMHC | 0.94 |  | -0.08 | 0.55 | -0.08 |
|  | 2000 | $CH_4$ | 1.31 |  | 1.76 | 1.39 | 1.71 |
|  |  | THC | 2.37 | 2.07 | 1.65 | 1.99 | 1.66 |
|  |  | NMHC | 1.06 |  | -0.11 | 0.60 | -0.05 |
|  | 2100 | $CH_4$ | 1.29 |  | 1.81 | 1.45 | 1.74 |
|  |  | THC | 2.52 | 2.12 | 1.86 | 2.13 | 1.75 |
|  |  | NMHC | 1.23 |  | 0.05 | 0.68 | 0.01 |

TABLE 29. COMPARATIVE EVALUATION AMBIENT AIR DATA.
August 28, 1976 - August 31, 1976

| Date | Time | Component | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
|---|---|---|---|---|---|---|---|
| 8-28-76 | 2200 | $CH_4$ | 1.30 | | 1.89 | 1.52 | 1.80 |
| | | THC | 2.59 | 2.12 | 1.92 | 2.11 | 1.77 |
| | | NMHC | 1.29 | | 0.03 | 0.59 | -0.03 |
| | 2300 | $CH_4$ | 1.29 | | 1.88 | 1.55 | 1.83 |
| | | THC | 2.57 | 2.16 | 1.92 | 2.14 | 1.70 |
| | | NMHC | 1.28 | | 0.04 | 0.59 | -0.07 |
| | 2400 | $CH_4$ | 1.50 | | 1.88 | 1.52 | 1.80 |
| | | THC | 2.68 | 2.01 | 1.90 | 2.02 | 1.72 |
| | | NMHC | 1.18 | | 0.02 | 0.50 | 0.00 |
| 8-29-76 | 0100 | $CH_4$ | 1.47 | | 1.88 | 1.53 | 1.82 |
| | | THC | 2.47 | 1.96 | 1.84 | 2.05 | 1.67 |
| | | NMHC | 1.00 | | -0.04 | 0.52 | -0.15 |
| | 0200 | $CH_4$ | 1.47 | | 1.88 | 1.54 | 1.81 |
| | | THC | 2.40 | 1.94 | 1.75 | 2.01 | 1.70 |
| | | NMHC | 0.93 | | -0.13 | 0.47 | -0.11 |
| | 0300 | $CH_4$ | 1.47 | | 1.86 | 1.52 | 1.81 |
| | | THC | 2.35 | 1.91 | 1.75 | 2.00 | 1.67 |
| | | NMHC | 0.88 | | -0.11 | 0.48 | -0.14 |

NOTE: From hour date $CH_4$ readings of MSA 11-2 have been corrected for an unexplained, abrupt baseline shift. Validity of data uncertain, but seems consistent with others.

## TABLE 29. COMPARATIVE EVALUATION AMBIENT AIR DATA.
August 28, 1976 - August 31, 1976

| Date | Time | Component | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
|---|---|---|---|---|---|---|---|
| 8-29-76 | 0400 | $CH_4$ | 1.43 | | 1.83 | 1.53 | 1.81 |
| | | THC | 2.35 | 1.89 | 1.76 | 2.00 | 1.67 |
| | | NMHC | 0.92 | | -0.07 | 0.47 | -0.14 |
| | 0500 | $CH_4$ | 1.42 | | 1.83 | 1.54 | 1.77 |
| | | THC | 2.31 | 1.81 | 1.73 | 1.97 | 1.63 |
| | | NMHC | 0.89 | | -0.10 | 0.43 | -0.14 |
| | 0600 | $CH_4$ | 1.42 | | 1.85 | 1.53 | 1.79 |
| | | THC | 2.30 | 1.90 | 1.74 | 1.97 | 1.72 |
| | | NMHC | 0.88 | | -0.11 | 0.44 | -0.07 |
| | 0700 | $CH_4$ | 1.47 | | 1.83 | 1.55 | 1.81 |
| | | THC | 2.28 | 1.81 | 1.74 | 1.98 | 1.67 |
| | | NMHC | 0.81 | | -0.09 | 0.43 | -0.14 |
| | 0800 | $CH_4$ | 1.43 | | 1.83 | 1.54 | 1.81 |
| | | THC | 2.26 | 1.88 | 1.71 | 1.97 | 1.67 |
| | | NMHC | 0.83 | | -0.12 | 0.43 | -0.14 |
| | 0900 | $CH_4$ | 1.48 | | 1.83 | 1.55 | 1.77 |
| | | THC | 2.25 | 1.79 | 1.74 | 1.97 | 1.67 |
| | | NMHC | 0.77 | | -0.09 | 0.42 | -0.10 |

## TABLE 29. COMPARATIVE EVALUATION AMBIENT AIR DATA.
August 28, 1976 - August 31, 1976

| Date | Time | Component | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
|---|---|---|---|---|---|---|---|
| 8-29-76 | 1000 | $CH_4$ | 1.48 | | 1.83 | 1.52 | |
| | | THC | 2.23 | 1.79 | 1.70 | 1.95 | |
| | | NMHC | 0.75 | | -0.13 | 0.43 | |
| | 1100 | $CH_4$ | 1.48 | | 1.81 | 1.51 | |
| | | THC | 2.21 | 1.79 | 1.67 | 1.93 | |
| | | NMHC | 0.73 | | -0.14 | 0.42 | |
| | 1200 | $CH_4$ | 1.47 | | 1.81 | 1.51 | |
| | | THC | 2.19 | 1.74 | 1.67 | 1.92 | |
| | | NMHC | 0.72 | | -0.14 | 0.41 | |
| | 1300 | $CH_4$ | 1.45 | | 1.78 | 1.50 | |
| | | THC | 2.23 | 1.70 | 1.70 | 1.93 | |
| | | NMHC | 0.78 | | -0.08 | 0.43 | |
| | 1400 | $CH_4$ | 1.45 | | 1.81 | 1.51 | |
| | | THC | 2.20 | 1.70 | 1.71 | 1.93 | |
| | | NMHC | 0.75 | | -0.10 | 0.42 | |
| | 1500 | $CH_4$ | 1.42 | | 1.77 | 1.51 | 1.73 |
| | | THC | 2.20 | 1.78 | 1.70 | 1.93 | 1.67 |
| | | NMHC | 0.78 | | -0.07 | 0.42 | -0.06 |

## TABLE 29. COMPARATIVE EVALUATION AMBIENT AIR DATA.
August 28, 1976 - August 31, 1976

| Date | Time | Component | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
|---|---|---|---|---|---|---|---|
| 8-29-76 | 1600 | $CH_4$ | 1.38 |  | 1.77 | 1.48 | 1.74 |
|  |  | THC | 2.21 | 1.72 | 1.70 | 1.93 | 1.66 |
|  |  | NMHC | 0.83 |  | -0.07 | 0.45 | -0.08 |
|  | 1700 | $CH_4$ | 1.37 |  | 1.77 | 1.49 | 1.73 |
|  |  | THC | 2.23 | 1.72 | 1.69 | 1.93 | 1.63 |
|  |  | NMHC | 0.86 |  | -0.08 | 0.44 | -0.10 |
|  | 1800 | $CH_4$ | 1.38 |  | 1.81 | 1.51 | 1.73 |
|  |  | THC | 2.21 | 1.70 | 1.72 | 1.93 | 1.63 |
|  |  | NMHC | 0.83 |  | -0.09 | 0.42 | -0.10 |
|  | 1900 | $CH_4$ | 1.40 |  | 1.81 | 1.51 | 1.73 |
|  |  | THC | 2.21 | 1.70 | 1.70 | 1.94 | 1.61 |
|  |  | NMHC | 0.81 |  | -0.11 | 0.43 | -0.12 |
|  | 2000 | $CH_4$ | 1.38 |  | 1.75 | 1.51 | 1.74 |
|  |  | THC | 2.25 | 1.79 | 1.70 | 1.95 | 1.67 |
|  |  | NMHC | 0.87 |  | -0.05 | 0.44 | -0.10 |
|  | 2100 | $CH_4$ | 1.48 |  | 1.81 | 1.51 | 1.77 |
|  |  | THC | 2.35 | 1.79 | 1.78 | 2.04 | 1.67 |
|  |  | NMHC | 0.87 |  | -0.03 | 0.53 | -0.10 |

TABLE 29. COMPARATIVE EVALUATION AMBIENT AIR DATA.
August 28, 1976 – August 31, 1976

| Date | Time | Component | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
|---|---|---|---|---|---|---|---|
| 8-29-76 | 2200 | $CH_4$ | 1.52 |  | 1.58 | 1.55 | 1.76 |
|  |  | THC | 2.52 | 1.92 | 1.94 | 2.13 | 1.77 |
|  |  | NMHC | 1.0 |  | 0.36 | 0.58 | 0.01 |
|  | 2300 | $CH_4$ | 1.74 |  | 1.98 | 1.71 | 1.95 |
|  |  | THC | 2.74 | 2.16 | 2.12 | 2.37 | 1.95 |
|  |  | NMHC | 1.0 |  | 0.14 | 0.66 | 0 |
|  | 2400 | $CH_4$ | 1.55 |  | 1.86 | 1.50 | 1.80 |
|  |  | THC | 2.23 | 1.83 | 1.74 | 1.93 | 1.70 |
|  |  | NMHC | 0.68 |  | −0.12 | 0.43 | −0.10 |
| 8-30-76 | 0100 | $CH_4$ | 1.55 |  | 1.81 | 1.56 | 1.77 |
|  |  | THC | 2.16 | 1.85 | 1.78 | 1.85 | 1.66 |
|  |  | NMHC | 0.61 |  | −0.03 | 0.29 | −0.11 |
|  | 0200 | $CH_4$ | 1.58 |  | 1.78 | 1.55 | 1.76 |
|  |  | THC | 2.16 | 1.85 | 1.76 | 1.81 | 1.66 |
|  |  | NMHC | 0.58 |  | −0.02 | 0.26 | −0.10 |
|  | 0300 | $CH_4$ | 1.74 |  | 1.86 | 1.63 | 1.85 |
|  |  | THC | 2.21 | 1.93 | 1.82 | 1.86 | 1.72 |
|  |  | NMHC | 0.47 |  | −0.04 | 0.23 | −0.13 |

TABLE 29. COMPARATIVE EVALUATION AMBIENT AIR DATA.
August 28, 1976 - August 31, 1976

| Date | Time | Component | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
|---|---|---|---|---|---|---|---|
| 8-30-76 | 0400 | $CH_4$ | 1.61 |  | 1.78 | 1.59 | 1.82 |
|  |  | THC | 2.12 | 1.96 | 1.76 | 1.78 | 1.67 |
|  |  | NMHC | 0.51 |  | -0.02 | 0.19 | -0.15 |
|  | 0500 | $CH_4$ | 1.65 |  | 1.81 | 1.59 | 1.77 |
|  |  | THC | 2.12 | 1.90 | 1.78 | 1.76 | 1.66 |
|  |  | NMHC | 0.47 |  | -0.03 | 0.17 | -0.11 |
|  | 0600 | $CH_4$ | 1.68 |  | 1.82 | 1.61 | 1.83 |
|  |  | THC | 2.16 | 1.90 | 1.80 | 1.83 | 1.70 |
|  |  | NMHC | 0.48 |  | -0.02 | 0.22 | -0.13 |
|  | 0700 | $CH_4$ | 1.68 |  | 1.84 | 1.59 | 1.81 |
|  |  | THC | 2.18 | 1.90 | 1.80 | 1.85 | 1.75 |
|  |  | NMHC | 0.50 |  | -0.04 | 0.26 | -0.06 |
|  | 0800 | $CH_4$ | 1.71 |  | 1.81 | 1.60 | 1.82 |
|  |  | THC | 2.21 | 2.04 | 1.88 | 1.91 | 1.72 |
|  |  | NMHC | 0.50 |  | 0.07 | 0.31 | -0.10 |
|  | 0900 | $CH_4$ | 1.61 |  | 1.81 | 1.58 | 1.79 |
|  |  | THC | 2.14 | 1.91 | 1.82 | 1.80 | 1.66 |
|  |  | NMHC | 0.53 |  | 0.01 | 0.22 | -0.13 |

## TABLE 29. COMPARATIVE EVALUATION AMBIENT AIR DATA.
August 28, 1976 - August 31, 1976

| Date | Time | Component | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
|---|---|---|---|---|---|---|---|
| 8-30-76 | 1000 | $CH_4$ | 1.65 |  | 1.81 | 1.58 | 1.77 |
|  |  | THC | 2.15 | 1.83 | 1.78 | 1.81 | 1.72 |
|  |  | NMHC | 0.50 |  | -0.03 | 0.23 | -0.05 |
|  | 1100 | $CH_4$ | 1.65 |  | 1.76 | 1.59 | 1.77 |
|  |  | THC | 2.10 | 1.79 | 1.74 | 1.74 | 1.75 |
|  |  | NMHC | 0.45 |  | -0.02 | 0.15 | -0.02 |
|  | 1200 | $CH_4$ | 1.61 |  | 1.77 | 1.56 | 1.74 |
|  |  | THC | 2.09 | 1.79 | 1.75 | 1.77 | 1.63 |
|  |  | NMHC | 0.48 |  | -0.02 | 0.21 | -0.11 |
|  | 1300 | $CH_4$ | 1.60 |  | 1.77 | 1.56 | 1.73 |
|  |  | THC | 2.07 | 1.79 | 1.75 | 1.77 | 1.61 |
|  |  | NMHC | 0.47 |  | -0.02 | 0.21 | -0.12 |
|  | 1400 | $CH_4$ | 1.58 |  | 1.76 | 1.55 | 1.73 |
|  |  | THC | 2.12 | 1.88 | 1.78 | 1.73 | 1.61 |
|  |  | NMHC | 0.54 |  | 0.02 | 0.18 | -0.12 |
|  | 1500 | $CH_4$ | 1.55 |  | 1.76 | 1.57 | 1.73 |
|  |  | THC | 2.18 | 1.96 | 1.78 | 1.76 | 1.61 |
|  |  | NMHC | 0.63 |  | -0.02 | 0.19 | -0.12 |

TABLE 29. COMPARATIVE EVALUATION AMBIENT AIR DATA.
August 28, 1976 - August 31, 1976

| Date | Time | Component | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
|---|---|---|---|---|---|---|---|
| 8-30-76 | 1600 | $CH_4$ | 1.53 |  | 1.71 | 1.55 | 1.71 |
|  |  | THC | 2.21 | 1.87 | 1.80 | 1.75 | 1.63 |
|  |  | NMHC | 0.68 |  | 0.09 | 0.20 | -0.08 |
|  | 1700 | $CH_4$ | 1.47 |  | 1.75 | 1.55 | 1.71 |
|  |  | THC | 2.21 | 1.88 | 1.82 | 1.73 | 1.63 |
|  |  | NMHC | 0.74 |  | 0.07 | 0.18 | -0.08 |
|  | 1800 | $CH_4$ | 1.45 |  | 1.76 | 1.55 | 1.73 |
|  |  | THC | 2.16 | 1.88 | 1.74 | 1.76 | 1.63 |
|  |  | NMHC | 0.71 |  | -0.02 | 0.21 | -0.10 |
|  | 1900 | $CH_4$ | 1.45 |  | 1.71 | 1.57 | 1.71 |
|  |  | THC | 2.21 | 1.88 | 1.75 | 1.74 | 1.63 |
|  |  | NMHC | 0.76 |  | 0.04 | 0.17 | -0.08 |
|  | 2000 | $CH_4$ | 1.52 |  | 1.86 | 1.58 | 1.82 |
|  |  | THC | 2.35 | 1.96 | 1.95 | 1.76 | 1.72 |
|  |  | NMHC | 0.83 |  | 0.09 | 0.18 | -0.10 |
|  | 2100 | $CH_4$ | 1.60 |  | 1.86 | 1.66 | 1.82 |
|  |  | THC | 2.44 | 2.16 | 1.90 | 1.85 | 1.80 |
|  |  | NMHC | 0.84 |  | 0.04 | 0.19 | -0.02 |

### TABLE 29. COMPARATIVE EVALUATION AMBIENT AIR DATA.
### August 28, 1976 - August 31, 1976

| Date | Time | Component | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
|---|---|---|---|---|---|---|---|
| 8-30-76 | 2200 | $CH_4$ | 1.68 | | 1.91 | 1.78 | 1.88 |
| | | THC | 2.35 | 2.13 | 1.97 | 2.05 | 1.80 |
| | | NMHC | 0.67 | | 0.06 | 0.27 | -0.08 |
| | 2300 | $CH_4$ | 1.68 | | 1.94 | 1.70 | 1.86 |
| | | THC | 2.37 | 2.24 | 2.05 | 1.93 | 1.72 |
| | | NMHC | 0.69 | | 0.11 | 0.23 | -0.06 |
| | 2400 | $CH_4$ | 1.78 | | 1.94 | 1.79 | 1.88 |
| | | THC | 2.46 | 2.23 | 2.05 | 1.99 | 1.77 |
| | | NMHC | 0.68 | | 0.11 | 0.20 | -0.11 |
| 8-31-76 | 0100 | $CH_4$ | 1.93 | | 2.01 | 1.75 | 1.95 |
| | | THC | 2.48 | 2.20 | 2.09 | 2.05 | 1.85 |
| | | NMHC | 0.55 | | 0.08 | 0.30 | -0.10 |
| | 0200 | $CH_4$ | 1.69 | | 1.86 | 1.71 | 1.89 |
| | | THC | 2.41 | 2.09 | 1.95 | 1.80 | 1.75 |
| | | NMHC | 0.72 | | 0.09 | 0.09 | -0.14 |
| | 0300 | $CH_4$ | 1.87 | | 1.94 | 1.71 | 1.96 |
| | | THC | 2.43 | 2.20 | 2.03 | 2.00 | 1.87 |
| | | NMHC | 0.56 | | | | |

## TABLE 29. COMPARATIVE EVALUATION AMBIENT AIR DATA.
August 28, 1976 - August 31, 1976

| Date | Time | Component | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
|---|---|---|---|---|---|---|---|
| 8-31-76 | 0400 | $CH_4$ | 1.81 |  | 1.91 | 1.71 | 1.91 |
|  |  | THC | 2.35 | 2.07 | 1.96 | 1.95 | 1.87 |
|  |  | NMHC | 0.54 |  | 0.05 | 0.24 |  |
|  | 0500 | $CH_4$ | 1.80 |  | 1.91 | 1.73 | 1.95 |
|  |  | THC | 2.35 | 2.09 | 2.01 | 1.95 | 1.87 |
|  |  | NMHC |  |  | 0.10 |  |  |
|  | 0600 | $CH_4$ | 1.87 |  | 1.96 | 1.75 | 1.91 |
|  |  | THC | 2.37 | 2.17 | 2.03 | 2.01 | 1.82 |
|  |  | NMHC | 0.50 |  | 0.07 | 0.26 |  |
|  | 0700 | $CH_4$ | 1.82 |  | 1.96 | 1.73 | 1.92 |
|  |  | THC | 2.36 | 2.23 | 2.00 | 2.01 | 1.82 |
|  |  | NMHC |  |  | 0.04 |  |  |
|  | 0800 | $CH_4$ | 1.84 |  | 1.96 | 1.79 | 1.91 |
|  |  | THC | 2.55 | 2.38 | 2.13 | 2.09 | 1.90 |
|  |  | NMHC | 0.71 |  | 0.13 | 0.30 |  |
|  | 0900 | $CH_4$ | 1.81 |  | 1.91 | 1.71 | 1.85 |
|  |  | THC | 1.94 | 2.28 | 2.03 | 2.01 | 1.85 |
|  |  | NMHC |  |  | 0.12 |  |  |

TABLE 29. COMPARATIVE EVALUATION AMBIENT AIR DATA.
August 28, 1976 - August 31, 1976

| Date | Time | Component | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
|---|---|---|---|---|---|---|---|
| 8-31-76 | 1000 | $CH_4$ | 1.77 |  | 1.81 | 1.70 | 1.83 |
|  |  | THC | 2.26 | 2.01 | 1.99 | 1.95 | 1.75 |
|  |  | NMHC | 0.49 |  | 0.18 | 0.25 |  |
|  | 1100 | $CH_4$ | 1.69 |  | 2.01 | 1.66 | 1.77 |
|  |  | THC | 2.14 | 1.90 | 2.03 | 1.81 | 1.67 |
|  |  | NMHC |  |  | 0.02 |  |  |
|  | 1200 | $CH_4$ | 1.68 |  | 1.77 | 1.66 | 1.74 |
|  |  | THC | 2.14 | 1.83 | 1.85 | 1.79 | 1.66 |
|  |  | NMHC | 0.46 |  | 0.08 | 0.13 |  |
|  | 1300 | $CH_4$ | 1.66 |  | 1.76 | 1.61 | 1.74 |
|  |  | THC | 2.12 | 1.79 | 1.82 | 1.76 | 1.63 |
|  |  | NMHC |  |  | 0.06 |  |  |
|  | 1400 | $CH_4$ | 1.65 |  | 1.77 | 1.62 | 1.76 |
|  |  | THC | 2.12 | 1.83 | 1.83 | 1.79 | 1.66 |
|  |  | NMHC | 0.47 |  | 0.06 | 0.17 |  |
|  | 1500 | $CH_4$ | 1.68 |  | 1.77 | 1.61 | 1.76 |
|  |  | THC | 2.09 | 1.77 | 1.75 | 1.73 | 1.66 |
|  |  | NMHC |  |  | -0.02 |  |  |

## TABLE 30. AVERAGE METHANE CONCENTRATION AND RATIOS OF INDIVIDUAL INSTRUMENT READINGS TO METHANE

| | | | Ratios (Instrument Value/Average) | | | |
|---|---|---|---|---|---|---|
| Date | Time | $CH_4$ Avg.(1) (ppm) | MSA 11-2 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
| 8/28/76 | 1600 | 1.55 | 0.94 | 1.10 | 0.89 | 1.07 |
| | 1800 | 1.56 | 0.93 | 1.10 | 0.89 | 1.08 |
| | 2000 | 1.54 | 0.85 | 1.14 | 0.90 | 1.11 |
| | 2200 | 1.63 | 0.80 | 1.16 | 0.93 | 1.11 |
| | 2400 | 1.68 | 0.90 | 1.12 | 0.90 | 1.07 |
| 8/29/76 | 0200 | 1.68 | 0.88 | 1.12 | 0.92 | 1.08 |
| | 0400 | 1.65 | 0.87 | 1.11 | 0.93 | 1.10 |
| | 0600 | 1.65 | 0.86 | 1.12 | 0.93 | 1.09 |
| | 0800 | 1.65 | 0.87 | 1.11 | 0.93 | 1.10 |
| | 1000 | 1.61 | 0.92 | 1.14 | 0.94 | ---- |
| | 1200 | 1.60 | 0.92 | 1.13 | 0.95 | ---- |
| 8/29/76 | 1400 | 1.59 | 0.91 | 1.14 | 0.95 | ---- |
| | 1600 | 1.59 | 0.87 | 1.11 | 0.93 | 1.09 |
| | 1800 | 1.61 | 0.86 | 1.13 | 0.94 | 1.08 |
| | 2000 | 1.60 | 0.87 | 1.10 | 0.95 | 1.09 |
| | 2200 | 1.60 | 0.95 | 0.99 | 0.97 | 1.10 |
| | 2400 | 1.68 | 0.92 | 1.11 | 0.89 | 1.07 |

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(1) Average from MSA 11-2, Beckman 6800, Bendix 8200, Bendix 8201 hourly average values.

## TABLE 30. AVERAGE METHANE CONCENTRATION AND RATIOS OF INDIVIDUAL INSTRUMENT READINGS TO METHANE (Continued)

| | | | Ratios (Instrument Value/Average) | | | |
|---|---|---|---|---|---|---|
| Date | Time | $CH_4$ Avg.(1) (ppm) | MSA 11-2 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
| 8/30/76 | 0200 | 1.67 | 0.95 | 1.07 | 0.93 | 1.06 |
| | 0400 | 1.70 | 0.95 | 1.05 | 0.94 | 1.07 |
| | 0600 | 1.74 | 0.97 | 1.05 | 0.93 | 1.05 |
| | 0800 | 1.74 | 0.99 | 1.04 | 0.92 | 1.05 |
| | 1000 | 1.70 | 0.97 | 1.06 | 0.93 | 1.04 |
| | 1200 | 1.67 | 0.96 | 1.06 | 0.93 | 1.04 |
| 8/30/76 | 1400 | 1.66 | 0.95 | 1.06 | 0.94 | 1.05 |
| | 1600 | 1.63 | 0.94 | 1.05 | 0.95 | 1.05 |
| | 1800 | 1.62 | 0.89 | 1.08 | 0.96 | 1.07 |
| | 2000 | 1.70 | 0.90 | 1.10 | 0.93 | 1.07 |
| | 2200 | 1.81 | 0.93 | 1.05 | 0.98 | 1.04 |
| | 2400 | 1.85 | 0.96 | 1.05 | 0.97 | 1.02 |
| 8/31 | 0200 | 1.79 | 0.95 | 1.04 | 0.96 | 1.06 |
| | 0400 | 1.84 | 0.99 | 1.04 | 0.93 | 1.04 |
| | 0600 | 1.87 | 1.00 | 1.05 | 0.93 | 1.02 |
| | 0800 | 1.88 | 0.98 | 1.05 | 0.95 | 1.02 |
| | 1000 | 1.78 | 1.0 | 1.02 | 0.96 | 1.03 |
| | 1200 | 1.71 | 0.98 | 1.03 | 0.97 | 1.02 |

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(1) Average from MSA 11-2, Beckman 6800, Bendix 8200, Bendix 8201 hourly average values.

## TABLE 30. AVERAGE METHANE CONCENTRATION AND RATIOS OF INDIVIDUAL INSTRUMENT READINGS TO METHANE (Continued)

| | | | Ratios (Instrument Value/Average) | | | |
|---|---|---|---|---|---|---|
| Date | Time | $CH_4$ Avg.[(1)] (ppm) | MSA 11-2 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
| 8/31/76 | 1400 | 1.70 | 0.97 | 1.04 | 0.95 | 1.04 |

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[(1)] Average from MSA 11-2, Beckman 6800, Bendix 8200, Bendix 8201 hourly average values.

TABLE 31. AVERAGE TOTAL HYDROCARBON CONCENTRATION AND RATIOS OF INDIVIDUAL INSTRUMENT READINGS TO AVERAGE

| | | | Ratios (Instrument Value/Average) | | | | |
|---|---|---|---|---|---|---|---|
| Date | Time | THC Avg.(1) equiv. ppm $CH_4$ | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
| 8/28/76 | 1600 | 2.13 | 1.11 | 0.93 | 0.76 | 0.92 | 0.77 |
| | 1800 | 2.05 | 1.10 | 1.05 | 0.77 | 0.93 | 0.77 |
| | 2000 | 2.07 | 1.14 | 1.00 | 0.80 | 0.96 | 0.80 |
| | 2200 | 2.21 | 1.17 | 0.96 | 0.87 | 0.95 | 0.80 |
| | 2400 | 2.17 | 1.24 | 0.93 | 0.88 | 0.93 | 0.79 |
| 8/29/76 | 0200 | 2.06 | 1.17 | 0.94 | 0.85 | 0.98 | 0.83 |
| | 0400 | 2.03 | 1.16 | 0.93 | 0.87 | 0.99 | 0.82 |
| | 0600 | 2.02 | 1.14 | 0.94 | 0.87 | 0.98 | 0.85 |
| | 0800 | 1.98 | 1.14 | 0.95 | 0.86 | 0.99 | 0.84 |
| | 1000 | 2.03 | 1.10 | 0.88 | 0.82 | 0.96 | ---- |
| | 1200 | 1.88 | 1.16 | 0.93 | 0.89 | 1.03 | ---- |
| 8/29/76 | 1400 | 2.00 | 1.10 | 0.86 | 0.97 | ---- | 1.23 |
| | 1600 | 1.95 | 1.14 | 0.87 | 0.99 | 0.85 | 1.26 |
| | 1800 | 1.95 | 1.13 | 0.88 | 0.99 | 0.84 | 1.28 |
| | 2000 | 1.97 | 1.14 | 0.86 | 0.99 | 0.85 | 1.26 |
| | 2200 | 2.15 | 1.17 | 0.90 | 0.99 | 0.82 | 1.21 |
| | 2400 | 1.97 | 1.13 | 0.89 | 0.98 | 0.87 | 1.20 |

(1) Average from all instruments operating.

TABLE 31. AVERAGE TOTAL HYDROCARBON CONCENTRATION AND RATIOS OF INDIVIDUAL INSTRUMENT READINGS TO AVERAGE (Continued)

| Date | Time | THC Avg.(1) equiv. ppm $CH_4$ | Ratios (Instrument Value/Average) | | | | |
|---|---|---|---|---|---|---|---|
| | | | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
| 8/30/76 | 0200 | 1.91 | 1.13 | 0.97 | 0.92 | 0.95 | 0.87 |
| | 0400 | 1.92 | 1.11 | 1.02 | 0.92 | 0.93 | 0.87 |
| | 0600 | 1.95 | 1.11 | ---- | 0.92 | 0.94 | 0.87 |
| | 0800 | 2.01 | 1.10 | 1.01 | 0.93 | 0.95 | 0.86 |
| | 1000 | 1.94 | 1.11 | 0.94 | 0.92 | 0.93 | 0.89 |
| | 1200 | 1.89 | 1.11 | 0.95 | 0.93 | 0.94 | 0.86 |
| 8/30/76 | 1400 | 1.91 | 1.11 | 0.98 | 0.93 | 0.90 | 0.84 |
| | 1600 | 1.94 | 1.14 | 0.97 | 0.93 | 0.90 | 0.84 |
| | 1800 | 1.89 | 1.15 | 1.0 | 0.92 | 0.93 | 0.86 |
| | 2000 | 2.01 | 1.17 | 0.97 | 0.97 | 0.87 | 0.85 |
| | 2200 | 2.14 | 1.10 | 1.00 | 0.92 | 0.96 | 0.84 |
| | 2400 | 2.18 | 1.13 | 1.02 | 0.94 | 0.91 | 0.81 |
| 8/31/76 | 0200 | 2.09 | 1.16 | 1.00 | 0.94 | 0.86 | 0.84 |
| | 0400 | 2.13 | 1.11 | 0.97 | 0.92 | 0.92 | 0.88 |
| | 0600 | 2.15 | 1.10 | 1.01 | 0.94 | 0.93 | 0.85 |
| | 0800 | 2.27 | 1.12 | 1.05 | 0.94 | 0.92 | 0.84 |
| | 1000 | 2.09 | 1.08 | 0.96 | 0.95 | 0.93 | 0.84 |
| | 1200 | 1.96 | 1.09 | 0.94 | 0.95 | 0.92 | 0.85 |

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(1) Average from all instruments operating.

TABLE 31. AVERAGE TOTAL HYDROCARBON CONCENTRATION AND RATIOS OF INDIVIDUAL INSTRUMENT READINGS TO AVERAGE (Continued)

| | | | Ratios (Instrument Value/Average) | | | | |
|---|---|---|---|---|---|---|---|
| Date | Time | THC Avg.[1] equiv. ppm $CH_4$ | MSA 11-2 | Beckman 400 | Beckman 6800 | Bendix 8200 | Bendix 8201 |
| 8/31/76 | 1300 | 1.94 | 1.09 | 0.94 | 0.94 | 0.92 | 0.86 |

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[1] Average from all operating instruments.

# APPENDIX C

## EVALUATION OF STRIP CHART RECORDERS USED IN COMPARATIVE INSTRUMENTAL EVALUATION

### INTRODUCTION

During the comparative evaluation of hydrocarbon analyzers, strip chart recorders (SCR) were used to record the experimental data. To assure that none of the data was unfairly biased by a faulty SCR, the operating characteristics of all the recorders were examined.

As recently as 1968, about 28% of those actively involved in analysis were using peak height as the mode of quantitation (35). The current Reference Method for measuring non-methane hydrocarbons (NMHC) makes no mention of SCR specifications, although an accurate NMHC analysis is practically impossible with a malfunctioning or improperly adjusted recorder.

The recorders used in the evaluation were the following:

1. A Hewlett-Packard 680,
2. Two Hewlet-Packard 7101B (they are differentiated by the final 4 digits of their serial numbers, -1295 and -1293),
3. A Varian G-4000,
4. A Linear Instruments 252A,
5. A Leeds and Northrup Speedomax XL610, and
6. A Honeywell Electrik.

The first five SCR's were supplied by EPA for the instrumental evaluation and the Honeywell and Leeds and Northrup SCR's were supplied by RTI.

### DESCRIPTION OF TESTS PERFORMED

Five parameters were of particular concern in evaluation of the performance of the recorders. The first of these was an examination of the zero drift of the SCR's by short circuiting the inputs and allowing the recorders to operate with no manual adjustments for a 68 hour test period. This reflects any ambient dependence of the recorder electronics and provides a check on the linearity of the chart drives over a long-period.

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The rise and fall times, defined as 10% to 90% (and vice versa) of full-scale transitions, were measured by applying a full scale, 0.1 Hz square wave from a Hewlett-Packard Model 3300A Function Generator to the recorder while using fast chart speeds. By measuring the difference in the 10% and 90% points and knowing the chart speed, good rise and fall time approximations can be made.

Deadband is defined as the amount of applied input necessary to produce a recorder deflection and was measured by connecting the recorder input to a Fluke Model 731A DC Transfer Voltage Source (calibration traceable to NBS). The 731A is capable of 1 μv resolution, and by changing the input voltage in small increments, the deadband was determined for the recorder scales used in the instrumental evaluation most frequently. Deadband is reported as a percentage of full scale.

Any recorder overshoot was noted when the full scale, square wave was being applied.

Finally, a small signal, 3dB frequency was determined by applying a sine wave from the Hewlett-Packard 3300A to the recorder inputs. The peak-to-peak excursions covered approximately 20% of the scale. The frequency was increased from 0.1 Hz to the point where the response was 0.7 that of the 0.1 Hz response. This frequency represents the 3dB frequency of the entire recorder electromechanical system and represents recorder frequency limitations.

## RESULTS AND DISCUSSION

The results of the evaluation procedure are given in Table 32.

The zero drift for the HP680, Linear Instruments 252A, and the Varian G6400 was so slight that only upper limit approximations were made. The drifts of the HP7101B recorders and the Honeywell recorder were measureable but were still very slight, being well within specifications. The zero drift of the Leeds and Northrup was impossible to determine because of the ink system produced a thick, smeared trace. The value given in Table 32 is a gross upper limit and the actual value is probably considerably less.

The rise time of the instruments is comparable (HP680 has only a 5 inch chart; thereby giving the lower value) as are the fall times. The Honeywell recorder did not have a variable chart speed, and rise and fall times could not be measured with the chart speed it did have.

Deadband values are comparable. The only recorder to show overshoot was the HP680 and this value was within manfacturer's specification (no effort was made to correct the overshoot). The 3dB points ranged from about 2 to 4.5 Hz.

All chart drives were linear except the Varian G4000 which was in need of maintenance.

## CONCLUSIONS

Based on the characteristics presented in Table 32 it appears that the reocrders are all comparable and introduced no unfair bias to the instrumental data obtained in the comparative evaluation.

TABLE 32. RESULTS OF RECORDER EVALUATION

| Instrument | Zero Drift (% of Full Scale) | Rise Time (msec) | Fall Time (msec) | Deadband (% of Full Scale) | Overshoot (% of Full Scale) | 3 dB Point (Hz) |
|---|---|---|---|---|---|---|
| HP 680 | $\leq 0.005$ | 250 | 125 | 0.1 | 2<br>(0.1 in.) | 4.5 |
| HP 7101B-1295 | 0.06 | 416 | 333 | 0.04 | None | 3.6 |
| HP 7101B-1293 | 0.08 | 417 | 416 | 0.02 | None | 3.4 |
| Linear Instruments 252A | $\leq 0.006$ | 317 | 127 | 0.08 | None | 1.9 |
| Varian G4000 | $\leq 0.005$ | 375 | 250 | 0.06 | None | 4.5 |
| Honeywell Electrik | 0.08 | --- | --- | 0.04 | None | 4.0 |
| Leeds & Northrup | | | | | | |
| Channel #1 | $\leq 0.25$ | 580 | 580 | 0.03 | None | 2.2 |
| Channel #2 | $\leq 0.25$ | 580 | 660 | 0.04 | None | 2.1 |

TABLE 32. RESULTS OF RECORDER EVALUATION

# APPENDIX D

## PROPOSED PROCEDURE FOR THE MEASUREMENT OF NON-METHANE HYDROCARBONS IN THE ATMOSPHERE

### 1.0 PURPOSE

In typical polluted air samples the principal hydrocarbon component, methane ($CH_4$), is usually more abundant than all other hydrocarbons combined. Methane levels range from a natural background of about 1.2 ppm (parts per million) to values as high as 10 ppm in highly polluted urban environments.[1] Since methane is inert in photochemical reactions, it is necessary to measure the methane background separately to permit an estimation of the non-methane hydrocarbon (NMHC) fraction which is reactive. The National Ambient Air Quality Standard for NMHC content in ambient air is 0.24 ppm as equivalent methane.[2] This equivalent methane value is measured in terms of the response of a flame ionization detector (FID) to NMHC relative to the FID response to $CH_4$.[3] Hydrocarbon analyzers must be capable of measuring the low NMHC levels relative to the high $CH_4$ background levels.

The purpose of this standard is to specify performance criteria and a uniform calibration procedure applicable to all analyzers designed for the measurement of NMHC concentration in ambient air. In addition, specifications for reagents are given. There is a brief discussion of possible sources of error. A more detailed discussion of error sources, instrumental design principles and recommended good practices for installation, maintenance and operation of NMHC analyzers is given in reference 4.

### 2.0 PRINCIPLES OF MEASUREMENT

As of the date of the issuance of this procedure, all instruments commercially available for measurement of methane and NMHC concentrations in ambient air use the FID to develop an electrical signal current which is related to the hydrocarbon content of the sample. The response factors--i.e., the unit current per unit of hydrocarbon concentration--depend upon operating conditions and the type of hydrocarbon species. In general, the response for a given hydrocarbon species is dependent upon the specific physical conditions of the FID used--i.e., the geometry, materials of construction, reagent composition and flow rates. Usually the instrument manufacturer specifies the reagent composition and the flow rates, which are specified either directly in terms of flows actually measuring during initial instrument setup or indirectly in terms of pressure regulator settings.

Several methods of separation, to distinguish methane from the non-methane hydrocarbon components in a sample to be analyzed, have been used or proposed. The most widely used have been based upon a difference technique, either batch or continuous. The batch technique routes an aliquot of sample through a stripper column which delays the passage of all hydrocarbons except methane. The methane fraction is rapidly eluted and passed on to the FID for quantification. Following methane elution, the stripper column is backflushed to remove the NMHC fraction, which is exhausted back to atmosphere. During this part of the cycle another aliquot of sample is introduced directly to the (same) FID to obtain a signal related to the total hydrocarbon (THC) content of the air. Both the THC and $CH_4$ signals are recorded on a strip chart recorder, usually in a bargraphic representation with recorder pen deflection proportional to the peak height of the respective signals. These are usually converted manually to equivalent concentrations, using calibration curves, and the difference taken to determine NMHC concentration in terms of equivalent $CH_4$ response.

In the continuous difference technique a sample stream is divided into two parts and routed to two FIDs to simultaneously measure the total hydrocarbon content (THC channel) and the methane content ($CH_4$ channel). The methane concentration is obtained by oxidation of all NMHC components on a catalyst bed prior to the FID for methane determination. The electrical signals of the THC channel and $CH_4$ channel are subtracted by analog circuitry to obtain the NMHC concentration. This NMHC signal and the methane signal are available for continuous recording.

Instead of graphical or analog subtraction to obtain NMHC content, a direct method may be used. This employs a stripper column to separate $CH_4$ for determination in an FID. In this design, however, the backflushed NMHC components are directed to the FID for a determination of the NMHC concentration directly. The $CH_4$ and NMHC signals are available in analog form on a recorder or in digital form for printout or storage for subsequent use.

Another method which avoids the problems of nonuniform response of the FID to various NMHC species is to oxidize the NMHC backflush fraction and then convert it to methane in a hydrogen stream over a hot catalyst.

## 3.0 PERFORMANCE SPECIFICATIONS

Assurance of data quality is based upon the ability of NMHC analyzers to meet or to exceed certain performance specifications[5] on range, lower detectable limit, sensitivity, precision and calibration stability. When these specifications are met, the accuracy of the measurements will be related in a well-defined manner to the accuracy of the analysis of reagent standards used for calibration.

### 3.1 Range

The range of the instruments used will depend upon the maximum concentrations of methane and NMHC normally encountered in the region to be monitored. For methane 10 ppm full scale is normally sufficient. Instruments which measure NMHC directly should have a maximum range of 5 ppm equivalent $CH_4$.

### 3.2 Noise Level and Lower Detectable Limit

Instrument noise, random fluctuations in output signal, determines the lower detectable concentration level for hydrocarbon concentrations. The noise level is defined as the standard deviation, S, of the fluctuations about a given signal level. The lower detectable limit is defined as twice the noise level, or 2 S.

For non-methane hydrocarbon measurements a noise level of 0.05 ppm equivalent $CH_4$ should be maintained. This permits a lower detectable limit of 0.1 ppm, or about 40% of the current air quality standard of 0.24 ppm for NMHC. Those instruments which rely on a difference of THC and $CH_4$ readings require lower noise levels since

$$R_{NMHC} = (R_{THC} - R_{CH_4}) \pm \quad S^2_{THC} + S^2_{CH_4}$$

where R indicates the "reading" (signal value) for the respective quantities and S indicates the standard deviation of fluctuations about R.

For equal noise levels of the THC and $CH_4$ signals, a noise level of 0.05 ppm for the NMHC indication requires a noise level of 0.035 ppm for these THC and $CH_4$ signals, with a consequent lower detectable limit of 0.07 ppm for each. Instruments which measure NMHC directly either through backflush, oxidation and re-forming to methane or by some other method, should have for both the NMHC and methane channel a maximum noise level of 0.05 ppm equivalent $CH_4$ and a lower detectable limit of 0.1 ppm equivalent methane.

### 3.3 Precision, Stability and Accuracy

Measurement precision, defined as the standard deviation of response to repeated injections of sample of the same concentration, should be 0.1 ppm equivalent $CH_4$, determined at an input sample concentration at 80% of full scale (80% span).

Zero drift is defined as the maximum average deviation from average baseline setting measured over both 12-hour and 24-hour consecutive periods with an input sample containing the minimum obtainable (i.e. nominally "zero") hydrocarbons in air (see Section 5.4) and with no adjustment of instrument electronic or pneumatic controls during these periods. Maximum zero drift should be equal to or less than a signal corresponding to 0.1 ppm equivalent $CH_4$ when the temperature of the room containing the instrument is maintained within the range of 20°C to 30°C.

Span drift is defined as the percentage change in response to an input sample at a concentration equivalent to 80% of span measured over a 24-hour period with no adjustment of instrument electronic or pneumatic controls. Maximum span drift should be equal to or less than 5% when the temperature of the room containing the instrument is maintained within the range of 20°C to 30°C.

The accuracy of measurement is dependent upon instrument precision, calibration stability, and the accuracy of analysis of the reagent gases used for calibration. At the upper end of the instrument scale the accuracy is determined by instrument precision, span gas analysis error and span drift and any analysis error for the "zero" reagent gas hydrocarbon content.

## 4.0 APPARATUS

Figure 1, a schematic of typical calibration apparatus, shows the suggested configuration of the components listed below. All components of the hydrocarbon transfer and dilution system should be of glass, stainless steel or other non-reactive material and should be free of trace hydrocarbon contaminants.

### 4.1 Flow Contollers

Devices should be capable of maintaining constant air flows or hydrocarbon mixture flows within ±2% of the required flow rate.

### 4.2 Pressure Regulators

Specially cleaned regulators for air cylinders and for hydrocarbon cylinders which contain no trace hydrocabons or other contaminants that would react with hydrocarbons should be used.

### 4.3 Mixing Chamber

The chamber should be constructed of glass or other nonreactive material and designed to provide thorough mixing of hydrocarbon calibration gases and diluent air.

### 4.4 Humidifier

A thermostated bubbler containing distilled water should be employed to obtain air streams of constant humidity.

### 4.5 Sample Manifold

The manifold should be constructed of glass or other non-reactive material and should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

## 5.0 REAGENT SPECIFICATIONS

In the following specifications "air" is defined as a gas mixture containing 21% ± 1% by volume $O_2$, with the balance, $N_2$. Rare gas (Ar, He, etc.) and $CO_2$ content should not significantly exceed normal concentrations in the atmosphere at sea level (about 330 ppm by volume). Total hydrocarbon content, methane pulse non-methane hydrocarbons, should not exceed 0.1 ppm equivalent $CH_4$. Water vapor content should be at or below that corresponding to -40°C dew point.

### 5.1 Fuel for Flame Ionization Detector (FID)

Fuel for the flame ionization detectors used for analysis should be hydrogen or a mixture of hydrogen and gas such as nitrogen or helium containing less than 0.1 ppm total hydrocarbons (THC) expressed as equivalent methane.

### 5.2 Support Air

Support air for the FID should have the composition defined as "air" and contain less than 0.1 ppm THC expressed as equivalent methane.

### 5.3 Carrier Gas

The composition of carrier gas depends upon the type instrument design used for analysis. Commonly either helium, nitrogen, air or hydrogen is used. Whichever gas is used, THC content should be less than 0.1 ppm equivalent methane.

### 5.4 Zero Gas

The gas mixture used for setting the baseline (zero level) of the instrument should be "air" of the composition defined above, containing less than 0.1 ppm THC equivalent methane.

### 5.5 Calibration Gases

The methane and THC channel of the analyzer should be calibrated by use of mixtures of $CH_4$ in "air" (of the composition described above). The calibration standard must be traceable to a National Bureau of Standards methane in air Standard Reference Material (SRM 1658 or 1659). A propane in "air" calibration standard is required for determining the NMHC response factor (see section 6.2) for the particular analyzer. This standard must be traceable to an NBS propane in air (SRM 1665 or 1666). Procedures for certifying the methane and propane cylinders (working standards) against the appropriate NBS traceable methane or propanes standards are given in reference 4. The cylinders should be rectified on a regular basis as determined by the local quality control program.

## 6.0 PROCEDURE

The analyzer should be installed on location preferably by the manufacturer or his authorized representative. If this is not done, installation and preparation for operation should be carefully performed by qualified instrumentation specialists following the analyzer manufacturer's instruction manual.

### 6.1 Initial Setup

The analyzer should be installed on location preferably by the manufacturer or his authorized representative. If this is not done, installation and preparation for operation should be carefully performed by qualified instrumentation specialists following the analyzer manufacturer's instruction manual.

### 6.2 Initial Calibration

Following preparation of the analyzer for operation and after stability of instrument temperature, fuel, carrier gas and support air has been achieved, calibration can be started. Because the ambient air water vapor content (humidity) may have an effect upon instrument response,[6] the calibration gases should be conditioned prior to introduction into the instrument. This can be accomplished by the use of a bubbler containing distilled water kept at a constant temperature by a thermostated bath. The bath temperature should be maintained at a temperature that provides an equilibrium partial pressure of water vapor corresponding to the relative humidity anticipated at the measurement site. For many sites a wide range of relative humidity values is encountered, varying seasonally and even diurnally. In these cases the calibration should be carried out at the upper and lower limits of water vapor content anticipated. These calibration curves, along with measurement of the actual water vapor content throughout the monitoring period, will allow interpolation to determine the actual calibration corresponding to the given water vapor content obtaining at the time of measurement.

With the humidifying bubbler adjusted to give the desired water vapor content, introduce the zero gas. Allow the analyzer output signal to stabilize and then adjust analyzer controls to obtain a zero reading on the output indicator. Depending upon instrument design and method of data collection and recording, the output indicator may be an analog meter, strip chart recorder, digital indicator or digital printout. Following setting of the zero level, which is performed for both instrument channels, introduce the nominal 80% full-scale methane calibration gas and adjust the analyzer $CH_4$ and THC span controls for the corresponding channels to obtain an output indication corresponding to the certified analysis of this calibration gas. Recheck zero and span until adjustments are no longer necessary. Then sequentially introduce intermediate value calibration mixtures of 10, 20, 40 and 60% of full scale. Plot the output values corresponding to the certifed analysis concentration numbers and construct a calibration curve. The response should be linear within ±1% of full scale. If the calibration points do not lie within this limit, the calibration gases may need replacement or there may be some equipment malfunction which should be isolated and corrected.

Using the same humidification level as for the calibration of the $CH_4$ and THC channel above, introduce a series of propane calibration mixtures at levels of 10, 20, 40, 60 and 80% of full-scale response. Plot the analyzer NMHC values corresponding to the certified analysis concentration numbers (as equivalent methane) and construct a NMHC calibration curve. The slope of this curve determines the NMHC response factor of the particular analyzer under calibration. If more than one humidity level is to be used, repeat the above procedures at each level.

### 6.3 Routine Operation

Following calibration, manufacturer's instructions should be followed to commence routine analysis operation. Performance should be checked for several cycles to assure that automatic operation is reliable before committing the instrument to unattended operation. Subsequent inspections at least every 72 hours and preferably every 24 hours should be made to verify continued satisfactory operation.

### 6.4 Routine Calibration

Periodic checks and adjustments as necessary, at least every 72 hours and preferably every 24 hours, or zero and span should be made to assure data quality. Some instrument manufacturers may offer automatic zero and span cycles as an option. When these are not used, manual calibration checks using span (nominal 80% full scale) and zero gases can be scheduled to coincide with routine maintenance tasks such as reagent replenishment. An operational log should be maintained to aid in identifying incipient problems with calibration stability.

## 7.0 QUANTIFICATION OF AMBIENT AIR HYDROCARBON LEVELS

### 7.1 Difference Methods

For the batch difference method the output indication pairs corresponding to total hydrocarbons (equivalent methane) and methane for a given cycle are converted to equivalent ppm methane in air directly from the calibration curve for the respective channels. The methane value is subtracted from the total hydrocarbon value and the difference is multiplied by the NMHC response factor to obtain the value of the methane equivalent to the non-methane hydrocarbons in the sample.

For the continual difference method the outputs corresponding to the methane channel and the NMHC channel are directly converted to equivalent $CH_4$ concentrations using the respective calibration curves for each channel.

### 7.2 Backflush Method

The output indication pairs corresponding to the methane and non-methane hydrocarbons, expressed as equivalent methane, for a given cycle are converted to ppm methane in air directly from the calibration curves for the respective channels.

### 7.3 Equivalent Mass Concentration

Conversion of the value of ppm methane in air obtained from the procedures above to an equivalent mass concentration of carbon in air is obtained by multiplying the ppm $CH_4$ by 0.654 to obtain equivalent carbon (as $CH_4$) in milligrams per cubic meter of air at 25°C and 760 ton.

## 8.0 SOURCE OF ERROR

Sources of error in environmental monitoring instrumental measurements are discussed in detail in reference 4. Some of these error sources of particular importance in hydrocarbon measurements are briefly pointed out below to aid in operator recognition.

### 8.1 Interferences

Other gas and vapor phase pollutants at the concentrations which are likely to occur in ambient air, with the exception of water vapor, do not interfere with this hydrocarbon measurement method. Water vapor can introduce measurement errors by altering flame ionization detector response. The magnitude of this effect can vary from instrument to instrument, depending upon design. Conflicting reports have been published in the literature. One report[6] has indicated that a change of over 4% in response may occur over the normal range from 40% RH to 100% RH at 25°C air temperature when the water vapor is injected directly with the hydrocarbon sample, as is done in those analyzer designs that use the difference method.

### 8.2 Zero Drift

Most commercial GC-type instruments incorporate electronic circuitry which automatically corrects for baseline drift when the instrument is working as designed. Usually this correction is updated once per measurement cycle when the instrument is used in the bargraphic mode. In addition, there are usually adjustments to set the zero position of the pen on the strip chart recorder. Instrument manufacturers specify the performance of these functions, usually expressed as a percentage of full-scale indication over some definite time period. The stability of these adjustments can be affected by many factors. Conformity with these specifications should be routinely checked in order to prevent gradual or catastrophic degradation of performance causing the generation of spurious data.

### 8.3 Span Drift

Most commercial instruments incorporate controls for adjusting the amplification factor of electronic amplifiers in order to obtain a desired output signal level (full scale indication) corresponding to a given input concentration. The stability of these adjustments, once made, is usually specified by the manufacturer as a maximum deviation, usually expressed as a percentage of full scale over some definite time period. This stability may be affected by many factors and should be routinely checked in order to prevent gradual or catastrophic degradation of performance causing the generation of spurious data.

### 8.4 Calibration Gases

The use of the calibration gases is required to allow adjustment of the analyzer zero and span controls in order to obtain a calibration curve. The specifications of these calibration gases are given in Section 4.

The calibration procdure is given in Section 5. Care should be exercised to assure that the calibration gases conform to the specifications. Gases should be ordered with an analysis certification by the supplier traceable to the National Bureau of Standards, Standard Reference Materials 1658, 1659 and 1660 as appropriate.

Pressure regulators, gauges and connecting tubing used with the calibration gases should be scrupulously clean to prevent the spurious introduction of unknown and uncontrolled amounts of hydrocarbons into the analyzer.

### 8.5 Support Gases

Specifications for fuel, carrier and combustion support gases are given in Section 4. Variable hydrocarbon content from tank to tank can cause baseline shifts. In analyzers that have automatic baseline correction, these shifts can be compensated.

### 8.6 Data Reduction

In the difference method, where peak heights are determined by measuring scale displacements and subtracting the methane value from the THC value, the occurrence of large values of methane and relatively small values of NMHC can introduce significant error in the determination unless exceptional care is exercised in the graphical measurements. Use of digital technqiues can alleviate this problem to the point where calibration stability of the FID and associated electronic signal processing circuitry is the limit.

The backflush method does not require a subtractive step; however, it may suffer from problems inherent with the strip chart recorder graphical reduction process. If the NMHC concentration is small, the corresponding pen displacement will be small and may not correspond to the actual value due to dead-band and backlash effects in the recorder pen servo-system. This problem can be alleviated by digital, signal processing techniques or by scale compression-expansion methods.

The sample temperature and pressure should be known in order to reduce the concentration to standard conditions. Errors in the measurement of these values can cause similar errors in the calculation of HC concentrations.

## 9.0 REFERENCES

1. _______________. Air Quality Criteria for Hydrocarbons. National Air Pollution Control Administration Publication No. AP-64. March 1970. Chapter 3.

2. _______________. Environmental Protection Agency, Title 40, Code of Federal Regulations. Part 50-National Primary and Secondary Ambient Air Quality Standards. Federal Register, 36, 8186. April 30, 1971.

3. _______________. Environmental Protection Agency, Title 40, Code of Federal Regulations. Part 50-Reference Method for Determination of Hydrocarbons Corrected for Methane. Federal Register, 36, 8198. April 30, 1971.

4. _______________. Technical Assistance Document for the Measurement of Non-Methane Hydrocarbons in Ambient Air. In draft form from the Quality Assurance Branch of the Environmental Monitoring and Support Laboratory.

5. _______________. Guidelines for Determining Performance Characteristics of Automated Methods for Measuring Nitrogen Dioxide and Hydrocarbons Corrected for Methane in Ambient Air. Environmental Protection Agency, Research Triangle Park, N. C. EPA Publication No. EPA-650/4-74-018. November 1974.

6. Harrison, J. W., M. L. Timmons, R. B. Denyszyn and C. E. Decker. Evaluation of the EPA Reference Method for the Measurement of Non-Methane Hydrocarbons - Final Report. EPA-600/4-77-033. Research Triangle Institute, Research Triangle Park, N. C. June 1977.